N.J.Marshall & Associates
Geochemical Consulting Services in Mineral Exploration.
Suite 2, 113 Forest Road, Hurstville, N.S.W. 2220 Australia Telephone (02) 570 6073

CONSULTANT'S REPORT TO

MT. LYELL MINING AND RAILWAY CO. LTD.

"GEOCHEMICAL EXPLORATION FOR BASE METALS,

WEST COAST TASMANIA"

N.J. Marshall
Geochemist

April 10,1979.

Distribution

Mt. Lyell,Queenstown - 2 copies.
Getty Oil Development Co.Ltd., - 1 copy.

ABSTRACT

The West Coast province occupied by Mt. Reid Volcanics has seen intensive activity in base metal exploration for Rosebery type, massive Pb-Zn mineralization, over many years.

In this rugged terrain with its high accessibility costs, "traditional" geochemical exploration has met with varying technical success, which is often compromised by the variety of soil conditions encountered. Follow-up costs are high, and greater discrimination is needed for geochemical targets prior to drilling.

Following an in-depth study of this area, several novel approaches to geochemical exploration are recommended. These have been tested by orientation sampling and should be applicable for any reasonably sized targets of the Rosebery type.

Cost savings should also be effected through increased sampling speed and efficiency using a suitable combination of the recommended procedure of phased (sequential) geochemical sampling. This approach may also reveal blind mineralization, and permits a faster coverage of areas.

The key features are:

1. heavy mineral reconnaissance drainage sampling.
2. analysis of Mn/Fe oxide coatings on stream pebbles. These have superior contrasts to conventional stream sediments, and permit effective sampling at a wider interval.
3. analysis of surface litter or A_0 organic samples where B horizon is difficult to collect consistently. These are effective for both reconnaissance and detailed grids, save the tedium of augering, and ensure a more consistent sampling medium than has previously been obtained.
4. analysis of "plumbing system" samples (wads and Fe oxides filling joints, fractures, and seepage areas). These may be a guide to blind mineralization.
5. analysis of rock samples for alteration assemblage elements and elements related to mineralization; Mn, Ba, Na/K ratios, Rb, F. Relative carbonate abundance and potassic alteration may also be logged in the field.
   Such rock analysis is applicable at both detailed scales (for following up base metal anomalies and assigning priorities to them) as well as broader scales. These elements give a diagnostic signature in footwall alteration for a considerable distance beyond the influence of sulfide mineralization.

6. field kits for on-site follow-up in regional prospecting of inaccessible areas.

Some interpretation is reported for areas visited, but the emphasis has been on more general aspects applicable to the region as a whole.

Routine grid results should be machine plotted as single element stacked profiles on transparent base map overlays. This is a superior approach to interpretation, using visual "pattern recognition" of anomalous trends, to the currently used approach.

To instigate this, a computerized data bank must be set up, to record all field and laboratory parameters and grid references in a systematic fashion. This will have other benefits also, in allowing data to be sorted, screened, retrieved and manipulated at will.

It is hoped that this very detailed write-up will act as a reference source to raise the cost-effectiveness of geochemical exploration in this region.

N. J. Marshall

N. J. Marshall

April 10, 1979.

289004

PART I - GENERAL TEXT

TABLE OF CONTENTS

page no.

SUMMARY OF MAJOR CONCLUSIONS AND RECOMMENDATIONS.

I. EXPLORATION.

Geochemical exploration in the joint venture areas is at several stages on various targets. Activities range from proposed new regions which have seen little previous work, through previously stream sediment sampled areas, to areas which have had detailed auger sampling carried out on grids. These are usually the result of follow-up of I P anomalies, and many soil anomalies have subsequently been complemented by costeaning and drilling.

1. Stream sediment reassessment.

A prime (winter activity) recommendation for future work is that all previous stream sediment data be compiled on standard (simple) drainage base maps as colored "worm diagrams" (one for each element). These should be overlaid on a photogeologic map base such as 1:40,000.

Careful interpretation and reassessment, with some re-sampling of critical areas may be needed to evaluate the validity of the data. In this context, previous stream sediment responses and anomaly distribution relative to known anomalous soil grids should be critically examined. This may indicate whether soil grids should have been extended, and whether known stream sediment anomalies adequately reflect known soil anomalies. If this is confirmed, then any untested stream anomalies in the old data would assume more priority for follow-up.

2. Phased geochemical exploration.

The section on "Sample Types on the West Coast of Tasmania" details all useful sample media which can be used, and their distribution, significance, collection, analysis and interpretat Specific details are discussed in the following sections on results of various orientation studies. This section also discus geochemical responses in these various media, and problems which may arise in field collection and interpretation. Detailed response diagrams, sample discriptions and analytical results ar given in the data volume accompanying this report.

Different data volumes have been prepared for the relevant Mt. Lyell and E Z orientation areas.

A general approach of phased geochemical exploration is suggeste for new or little worked areas, following the sequence developed in the section on "Sample Types".

Work on areas at a higher stage of activity (detailed soil grids may by-pass the earlier, more regionally oriented phases listed below, and procede where warranted to higher level phases of follow-up.

These include rock sampling for alteration element assemblages to classify mineralization (Rosebery type) and to trace the source of hydromorphically displaced anomalies (those lacking bedrock mineralization).

3. Geochemical Exploration Sequence.

The following steps list the complete geochemical exploration sequence for the region:

1) Heavy Mineral Panning.

Constant sized samples should be panned to a standard volume as a regional reconnaissance program. Sampling should be carried out from readily accessible sites at the necks or confluences of several major drainage basins, representing several sq. km. of watershed.

Examination of the concentrates by binocular microscope for mineral assemblages is then carried out. The samples are also examined by ultraviolet lamp for fluorescent minerals such as scheelite.

Any magnetite should be removed, weighed and submitted as a separate sample for emission spectrographic analysis for Cu, Pb, Zn, Ag, Bi, Co, Ni, Cr, Ba, Mn, Ti, V, Mo, and Nb., and results normalized to relative magnetite abundance.

The non-magnetic fraction should be analyzed by emission spectrograph for Cu, Pb, Zn, B, Ba, Sn, W, Cr, Nb, Ti, Zr, and Mo.

Data are best interpreted with the aid of a regional photogeologic base map with drainage overlay at the same scale.

2) Mn and Fe oxide coatings on stream pebbles.

Rather than traditional stream sediment sampling, collection of oxide coated stream pebbles, and analysis by hydroxylamine leach on the uncrushed material is proposed.

Orientation studies have conclusively demonstrated that pebble coating surveys give superior contrasts and probably longer dispersion trains compared to conventional stream sediments, and the problem of finding sufficient -80# material is overcome.

Sampling can probably be carried out at 1 km intervals, even along major streams, although of course sample density should be dictated by access, as all tributaries encountered during a traverse should be sampled.

An orientation study proposed along Itat Ck., draining the Beatrice prospect, should give further information on the length and intensity of anomalous dispersion, on which to base future surveys.

The leach solutions should be analyzed routinely by atomic absorption for Cu, Pb, Zn, Mn, Fe, and Co. Initially the Cu, Pb, Zn data should be plotted and examined for obvious anomalies, rather than using ratios.

Splits of the samples should be retained so that anomalous samples can be treated by acid leach (50% HCl) and re-analyzed for acid soluble Ba (by AAS), Ag and arsenic.

3) Stream sediment samples.

Because the prime exploration cost is access, conventional -80# stream sediment samples (as a composite from several adjacent sites) should be collected in conjunction with the pebble samples. (or where pebble coatings are not available.)

These should be analyzed for "total" Cu Pb Zn Mn Fe Ni and cold extractable (1 N HCl) Cu Pb Zn Mn, by atomic absorption.

Anomalous samples only should be re-analyzed for As, Ag and Ba.

Both total and Cx results should be plotted on a series of separate base drainage maps. The former are useful in reflecting combined effects of mineralization and lithologic variation (for "Mapping") whilst the Cx results are simpler to interpret for mineralization. They also tend to give higher contrast anomalies in this environment of chemical weathering.

Interpretation should be based on colored "worm diagrams" as drainage overlays to a photogeological map base.

Recording data on a computer accessible file will aid final interpretation because of the ease with which populations can be classified according to drainage basin lithology.

4) Stream sediment and pebble coating follow-up.

In areas of difficult access, field kits are proposed to enable follow-up to proceed in situ, and define the limits of the anomaly.

Instructions on preparation and use of a simple total heavy metals field kit are given in Appendix A.

Further follow-up, involving ridge and spur, and base of slope soil sampling, can also be done with these kits using non-organic soil components.

5) Regional soil sampling.

Sampling of surface litter, A_0 or A_1 horizons (whichever is most prevalent) is recommended on semi-cut lines.

This is particularly important in critical areas where an adequate drainage network is lacking.

Samples should be taken at intervals of 50 meters on parallel lines from valley to top of each ridge, at approximately 200 meter line spacing.

Lines should favour breaks in slope (parallel to contours), commencing above creek banks, with the object of locating hydromorphically displaced anomalies.

These would be a "lead-in" to more detailed systematic grid sampling, followed by augering, costeaning and drilling.

Thus much tedious and expensive systematic auger sampling of barren areas would be avoided, allowing coverage of the E L's to proceed at a more cost-effective rate.

Such sampling would be particularly rapid if the point location equipment discussed in this report proves practicable in field use, as formal line cutting and pegging would be minimized. These samples should be wet-ashed (perchloric/ nitric acids) and the elements Cu Pb Zn Mn determined by AAS. Anomalous samples to be re-analyzed for Ag Ba and As.

6) Regional wad and talus sampling.

Any samples of Mn wad formed in seepages, and -80# samples from the base of talus slopes, should be collected and sampled during the course of the regional soil sampling. Analysis of wad should include the above elements plus Co.

7) Reconnaissance rock sampling.

Rock samples, particularly from favourable stratigraphic horizons or where tectonically disturbed and visibly altered, should be sampled and analyzed for elements characteristic of the Rosebery assemblage.

This will aid in selecting favourable zones for mineralization, as the Hercules orientation study has demonstrated that bedrock, wallrock alteration signatures extend far beyond the limits of base metal anomalous values in the bedrock.

Where bedrock base metals are anomalous, the alteration assemblage may help classify the area for the purpose of assigning priorities.

In the field, a Mn association (staining) should be looked for (Hercules, Beatrice and Henty River type). Carbonate presence and abundance can be readily logged in the field with the use of acid.

A portable gamma ray spectrometer used in the field can "map" zones of higher potassium content.

The presence of fluorite, tourmaline, sphene and barite is an important guide to ore proximity.

Rock samples should be analyzed for Cu, Pb, Zn, Mn and in addition K, Na, Rb, and Fe. These can be done by HF/ aqua regia attack and atomic absorption. Details are given elsewhere in this report. Ba, B, Zr, Ti are best scanned by emission spectroscopy, with Ba re-analysis by XRF where more accuracy is desired.

Arsenic should also be determined (from AAS solution digest), and fluorine run by alkaline fusion and selective ion electrode.

The most diagnostic parameters are likely to be high Ba, B, Rb, and F, with decreasing Fe, increasing Mn, and increasing K/Rb and K/Na ratios approaching ore. High carbonate is also important.

8) "Plumbing system samples".

These are useful for detecting blind mineralization, particularly in glacial debris covered areas.

Samples of ironstone and Mn wad in seeps and as fracture fillings should be analyzed by an acid dissolution procedure and AAS for Cu, Pb, Zn, Mn, Fe, Co, Ba. Anomalous samples to be re-analyzed for Ag and As.

9) Detailed rock samples.

These are applicable in costeans, drill core, outcrops among soil grids, and auger bedrock chips as soil grid follow-up.

They are necessary in locating the bedrock source of soil anomalies, particularly where hydromorphic dispersion has caused a displacement of anomalous soil values downslope.

The same philosophy applies as for reconnaissance rock samples, and the same element assemblage should be run as discussed above.

Plumbing system sampling is also applicable at the detailed, follow-up stage, particularly in areas of thick glacial cover.

10) Detailed soil grids.

A wide variety of soil types is developed on both glacial debris and bedrock throughout this region, and causes complications with varying backgrounds and geochemical response.

The types of soils are discussed at length in the following section on "Sample Types", and some typical profiles are illustrated in the text and in the relevant sections on specific orientation sites.

Appendices to the orientation work describe individual samples collected.

There has been some confusion on soil classification in previous sampling, and in some areas attempts to hand auger to bedrock in difficult terrain have added to this confusion. For example, " C horizon " bedrock chips were encountered and the sample then sieved to -80#, resulting in B horizon samples, or augering has been stopped by boulders and C horizon assumed when the sample is still in the A profile.

Field crews should be instructed to recognize soil types, if possible, with the aid of reference samples.

Soil variations should be mapped prior to final interpretation of grids.

In areas where B horizon is readily and consistently available, this should be sampled in preference to C horizon, which is strictly <u>weathered</u> bedrock. Fresh bedrock (D horizon) is more common and can give rise to erratic values requiring very close sampling. Bedrock sampling is only necessary at the final stage of follow-up for siting drill targets.

B horizon samples should be analyzed by aqua regia or perchloric/nitric digests, and Cu Pb Zn Mn determined by AAS. Anomalous zones should be re-analyzed for the same elements via a 0.5 N HCl cold extraction, to help diagnose hydromorphically displaced anomalies.
Anomalous samples should also be tested for Ba Ag and As.

In complex sub-areas where B horizon is not consistently available, it is preferable to sample the surface litter, A_0 or A_1 horizons. The advantage of this approach is that difficult and time consuming augering is minimized.

These should be analyzed by a wet ash ($HClO_4/HNO_3$) procedure for Cu, Pb, Zn, Mn, with re-analysis of anomalous samples for Ba, Ag and As. With A_0 sampling, care must be exercised to maintain a constant organic/inorganic ratio, or else the variable organic component must be allowed for.

11. Hydromorphic Soil Anomalies.

In this steep terrain with high rainfall, anomalies due to chemical dispersion downslope can be expected. Movement away from the bedrock source can occur for considerable distances (300 meters at W. Hercules).

Thus all anomalous zones in soils should be followed up-slope for a mineralized bedrock source, if the source cannot be located in underlying bedrock.

The following section on "Sample Types" details methods of recognition and follow-up of displaced soil anomalies.

II DATA PLOTTING FOR INTERPRETATION.

1. Stream sediments and pebble coatings.

These should be located on aerial photographs, using stereoscopy, and sample numbers transferred to simple drainage base maps showing cultural features. Maps should be transparent overlays to a photogeologic base map.

A series of separate colored "worm diagrams" of arbitrary anomalous drainage for each element should be prepared after single element raw values are plotted (preferably by machine). This will serve for preliminary interpretation during work progress.

Final interpretation will use the same maps with single element raw data values, except that the colored anomalous "worm trails" are drawn in using locally adjusted, variable thresholds at each point. This is done by using a computerized data bank to sort samples into populations according to local lithologies and drainage basin. More sophisticated data processing and analysis may be desirable in the final stages, to extract the maximum information from the multi-element data, including geologic variation.

2) Soil grids.

These should be machine plotted as simple stacked profiles using vertical bars to designate sample position and relative intensities of values. The profiles must be plotted with their true spatial relationships preserved, on transparent overlays to the geologic map base.

Separate overlays should initially be prepared for the elements Cu, Pb, Zn, Mn.

Visual pattern recognition of these map profiles overlaid to geology is probably the most effective way to interpret data, by drawing in anomalous zones. This technique goes some way toward compensating for changes in background due to lithologic and soil variations.

The present system of manual plotting multiple data values at each site gives little visual impact and is confusing in detail.

Coloring in spot values and contouring them tends to assume a constant background and may be distorting in detail, especially where shifting backgrounds occur.

A quotation has been obtained for this plotting, and is approximately $660 per series of 4 A_0 map sheets covering approximately 1000 sample points. This is a minor interpretation cost relative to the overall exploration effort.

It is recommended that a trial plotting exercise be carried out on the N E quadrant of the Mt. Lyell White Spur Grid.

III DATA BANK.

For routine grid plotting and interpretation of regional stream sediment surveys a computerized data bank is highly desirable.

The present system of recording data would be very time consuming and prone to error if put on computer.

Therefore combined field and lab. data sheets should be instituted, so that all parameters additional to sample no., grid reference and analytical results can be stored, sorted or retrieved (listed) at will.

Discussions have been held on this aspect with both joint venture operators and it was agreed that forms which are flexible, practical and simple to use should be designed for handling their requirements.

These will be prepared and issued separately.

IV LABORATORY.

There may be an increased work load on the Mt. Lyell laboratory if it is to undertake the greater variety of analyses recommended.

Alternatively, increased cost would be incurred if the work is done by custom laboratories, as is the practice for E Z.

There are, however, advantages in time, convenience and cost in carrying out as much work as practicable "in house". The Mt. Lyell laboratory, although primarily funded as a mine lab. is competently staffed and reasonably well equipped to carry out most of the recommended analyses.

Some upgrading of facilities, such as installation of a good fume cupboard and purchase of a small jaw crusher is recommended.

With acquisition of several minor items of glassware, suitable test tube racks and labor-saving devices such as an automatic dilutor and dispensing pipettes, geochemical throughput could be significantly increased through greater efficiency.

A few days on-site training is recommended to introduce a more "batch production oriented" attitude to geochemical analysis without sacrificing accuracy.

Some training is also recommended for new techniques including analysis for elements not currently determined on a high throughput basis.

It may be desirable for both joint venture operators to pool resources toward establishing a joint geochemical analysis facility at Mt. Lyell.

Any increased analytical costs should be more than offset by the more cost-effective phased sampling procedures recommended above.

II. SAMPLE TYPES ON THE WEST COAST OF TASMANIA.

Resulting from orientation studies and field inspection of both joint venture areas, the following sample types are suggested as being the most useful at varying stages of geochemical exploration.

II 1. Reconnaissance Drainage Basin Studies. - heavy mineral panning.

1) Collection, plotting and recording data.

The most rapid assessment of mineralized drainage basins can be done at the reconnaissance scale by heavy mineral panning of drainage basins, typically representative of up to 10 sq. km. in this environment of rugged topography, complex drainage and high dilution.

Fig. A illustrates a typical area of about 20 sq.km. for which up to 12 heavy mineral sites could be sampled. Such sampling density should be adjusted according to the geological and drainage complexity, and the potential for mineralization within parts of each exploration licence.

Initially, samples should be collected at readily accessible sites from the mouths of major drainage basins.

Samples should be wet screened to about -10# from several composite sites across the stream bed, and every effort should be made to start with a constant sized sample and pan slowly and carefully to a "grey fraction" (crude concentrate) of constant volume. eg.) a bucketful panned down to a 20 ml plastic vial full. "Overpanning" to favor only the heaviest grains, as for gold panning, should be avoided.

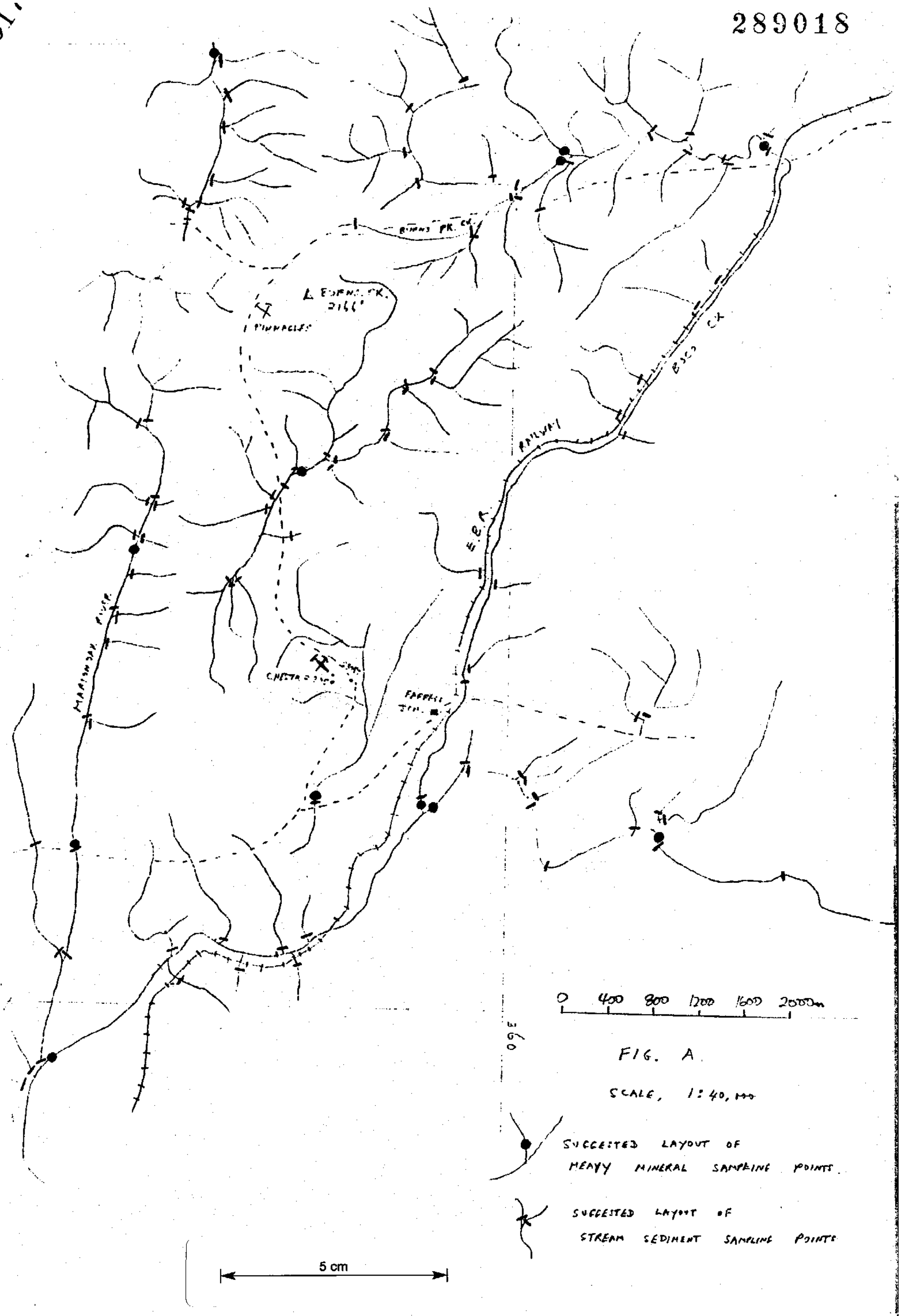
Sampling should be carried out in the portions of streams of approximately constant hydraulic load (eg. predominant fist sized cobbles), and the predominant float lithologies noted.

This can give a knowledge of rock type distribution upstream in poorly mapped areas, and also serves to check on geological contacts and lithologies in mapped areas.

Positioning should be done on aerial photographs in the field, with localities transferred to simplified base maps such as fig. A, showing only drainage, cultural features and the metric grid.

Prints of topographic base maps, showing contours are too confusing and should be avoided.
All stream parameters (width, contamination upstream etc.) should be noted for subsequent computer coding.

289018


BURNS PK. CK.
EVANS PK.
PINNACLES
MARIANDAN RIVER
E.S.A. RAILWAY
ESCO CK
0 400 800 1200 1600 2000m
FIG. A.
SCALE, 1:40,000
SUGGESTED LAYOUT OF HEAVY MINERAL SAMPLING POINTS.
SUGGESTED LAYOUT OF STREAM SEDIMENT SAMPLING POINTS
5 cm

2) Examination.

Initially, the concentrate samples should be examined at base with a binocular microscope, noting relative abundance of any unusual minerals.

The samples should be examined by ultraviolet lamp for fluorescent minerals such as scheelite.

Samples should then be despatched for fine grinding in a small mill, (such as a Spex mill) and analyzed by semiquantitative emission spectroscopy for: Cu, Pb, Zn, B, Ba, Sn, W, Cr, Nb, Zr, Ti.

3) Analysis of magnetite fractions.

If on binocular examination, magnetite is seen, this should be separated out with a hand magnet and weighed. The magnetic concentrate fraction should be finely crushed, and the following elements analyzed by emission spectrograph: Cu, Pb, Zn, Ag, Bi, Co, Ni, Cr, Ba, Mn, Ti, V, Mo, W and Nb. Results can be normalized to relative magnetite abundance if the panned fractions are constant.

W. Overstreet of the USGS (pers. comm,1971) in a study of a large area of Alaska successfully identified every one of 24 known Cu deposits, often 10 miles downstream from mineralization, using trace elements in magnetite.

The attached Appendix C details results of this survey, and gives some supplementary information.

Similarly, a study by Theobald, Overstreet and Thompson (1967) on "Minor Elements in Alluvial Magnetite from the Inner Piedmont Belt, North and South Carolina" (USGS Prof. Paper 554-A) states:

1) " a general partition of many of the trace elements favours magnetite over most other rock-forming minerals"

2) " the amount of metal attracted and retained by the magnetite will be strongly influenced by the amount of metal available. The availability of the metal is controlled by the absolute quantity of metal in the system, the nature of the system, and the nature of the individual elements".

3) "magnetite, particularly separates from alluvium, is an almost ideal medium for the study of the distribution of trace elements on a regional scale - a form of geochemical census".

4) " stream sediments, however, vary in metal content not only with the metal content of bedrock in the drainage basin but with erosion, transportation, and sedimentary history of the sediment. The effects of this variation are minimized, however, because only a single component of the sediment, magnetite, is used".

5) " there can be no doubt from the data presented that the regional distribution of some trace elements can be studied by the analysis of detrital magnetite".

The non-magnetic heavy mineral concentrates will serve as regional samples for Sn, and W mineralization.
Barium and boron contents will serve to outline zones of favourable host rock lithology for Rosebery type mineralization. These should be followed up by closer spaced drainage sampling using stream sediments and pebble coatings.

Conventional stream sediment samples and pebble coatings should also be collected at each heavy mineral site.

II. 2. <u>Detailed Drainage Basin Studies.</u>

<u>Stream Sediments.</u>

1) Collection and analyses.

In this environment of chemical weathering and rapid dilution, -80# stream sediments should be collected at fairly close intervals, and analyzed for "total" ($HClO_4/HNO_3$) Cu, Pb, Zn, Mn, Fe, Ni (AAS) and cold extractable (1 N HCl) Cu, Pb, Zn, Mn (by AAS).
Anomalous Cu Pb Zn values should be re-analyzed for As Ba and Ag. The total base metal values will tend to reflect the combined influence of lithologic variation and mineralization, and thus result in overlapping populations. Some weak anomalies may be masked by higher background values due to changing lithologies.

Nevertheless, the total base metal values, supplemented by Mn, Fe and Ni, can give some insight into up-drainage lithologies and changing backgrounds if careful interpretation is carried out, aided by sophisticated techniques such as factor analysis. This can aid regional mapping in unknown areas.

The cold extractable values are a more direct indicator of chemical dispersion from mineralization, and are less sensitive to lithologic variation. Anomalies due to mineralization will tend to have Cx values approaching total values.

2) Recording Data.

As with heavy mineral sampling, stream parameters including stream order, width, dominant lithologies in pebbles and cobbles, upstream contamination etc. should be noted. These should be coded onto computer compatible forms with analytical results to provide a systematic data bank. This can be updated at will if follow-up sampling or extra analyses are carried out.
The data bank would serve as the basis for future more sophisticated interpretation procedures (regression on Mn, sorting backgrounds into lithologic groups, factor analysis etc.)

3) Sample density.

All stream systems, including those draining glacials, should be sampled at approximately 1 km intervals.

Large streams should also be sampled to provide average background data.

Each sample should consist of a composite of several sites across and along the stream, placed in the one pre-numbered wet-strength Kraft envelope, with sample no. recorded on aerial photos for transference to drainage base maps.

The actual sample density should vary with geologic complexity (presence of fault zones, favourable contacts etc.), which is roughly proportioned to the locus for any likely mineralization.

Sample density should always be guided by practical considerations of access (ie. the costly component of exploration). Thus <u>all</u> side tributaries should be sampled if encountered during a traverse. Fig. A gives a suggested sampling layout for close coverage of a complex area containing known mineralization - this is an example only (area is outside E L).

In areas where coarse gravels predominate, fine fractions may collect under the roots of moss-covered stream boulders, but this type of sample should be noted,as organic enrichment may occur.

In routine survey, it may prove convenient to pre-number sample sites on aerial photographs and Kraft envelopes, and insist that field assistants flag each site with tape.

4) Duplicate sampling for errors.

During the course of a survey at least 30 regular, easily accessible sites should be re-sampled en route by different operators throughout the season, and submitted as new analyses.

Subsequent computer "analysis of variance" will establish total analytical + sampling error. This can prove useful for investigating weaker anomalies during second-pass follow-up, as an "error band" can be assigned around each threshold value in each lithology.

5) Progress Maps.

All access tracks such as timber cutting trails, as well as cultural features and known mineralization upstream should be located on the simplified drainage base maps using air photographs and local knowledge.

During the progress of sampling, colored "worm diagrams" using a scheme such as red, yellow, green for strong, moderate and weak values (tentatively assigned) should be used to monitor progress of the survey.

6) Anomaly follow-up.

All isolated anomalies should be re-sampled, preferably with the aid of field kits.

Closer fill-in stream sediment sampling is advised around anomalous areas to delineate their true limits, with the aid of stereo air photographs. In the author's experience, soil grids are often put in as follow-up at too early a stage, such that the grid is too large, or needs to be progressively extended when anomalies are not closed off.

At this follow-up stage, soil sampling of ridges and spurs, as well as along breaks in slope (above and parallel to creek banks) is recommended in conjunction with detailed stream sediment sampling. Any talus slopes should also be sampled at their base, as well as "plumbing system samples" such as Mn wad, and rock samples for alteration elements, at this stage.

Having ascertained the limits of the anomaly, the next stage is grid sampling, guided by geological and geophysical parameters.

Finally, it is desirable to keep a -20+80# fraction of the washed stream sediment mounted on chip cards, for subsequent binocular microscope examination of drainage lithology at each site.

II. 3. Detailed Drainage Basin Studies.

Mn/Fe coated pebbles.

1) Introduction.

Analysis of the soluble (reactive) stream sediment coatings in stream pebbles has been reported in the recent North American literature and at recent symposia of the Association of Exploration Geochemists, but has been ignored in this country. Key references include those by Whitney (1975), Carpenter et al (1975), Chao and Theobald (1976), Carpenter and Hayes (1978), Carpenter et al (1978), and Carpenter (1978, Golden, Colorado AEG symposium).

The principle of the method is that iron and manganese in solution will precipitate on increase in Eh and pH and coprecipitate trace elements in solution, onto any convenient surface.

This occurs when reduced, humic acid rich waters such as occur in the West Coast Tasmania region, are oxidized in shallow swift-flowing streams flowing over shingles. Aeration causes precipitation of Fe and Mn oxides onto pebble surfaces, via oxidation of Fe^{2+} and Mn^{2+} ions in solution. Fe oxide precipitation occurs first. In partially buried pebbles, the upper, exposed surface is often coated with black Mn oxides while the lower surface, if under water and in contact with organic matter, is clean, (reducing conditions).

The process of precipitation and scavenging of metals in solution from the stream water (ie. coprecipitation of chemically dispersed elements) is akin to the process of gossan formation, and the amount of scavenging is proportional to the amount of metal available. Thus analysis of coatings reflects the amount of metal in ground-water entering the stream.

This phenomenon has long been known in analytical chemistry, where, for example, trace elements including gold in sea water can be determined by adding Fe or Mn as a carrier to a large volume, followed by precipitation, collection and analysis of the solid phase. Manganese nodules in deep-sea sediments are a natural analog.

2) Advantages.

The main advantage of this technique is that it gives superior anomaly contrast and hence detectable anomalies at wider sample intervals, compared to conventional stream sediments where dilution by barren material is a problem. Sampling is also more constant, and the technique is reported as useful in glaciated terrain. This is because only hydromorphic, not mixed hydromorphic and clastic, components are favoured.

3) Analysis.

The samples are leached in a cold extractant such as hydroxylamine hydrochloride solution. This is a selective extractant of Mn, due to its reducing action.
Numerous other extractants have been proposed, and a thorough evaluation of which is best in this environment would require extensive laboratory trials. This is best done on orientation sampling proposed along Itat Ck., draining the Beatrice Prospect. (Mt. Lyell E L).

4) Orientation Results.

These orientation studies have demonstrated that even apparently Fe coated pebbles (red-brown) rather than black Mn coated ones give excellent contrasting anomalies - eg. at Sock Ck., and around the Hercules mine workings.

Carpenter (pers. comm. 1978) proposed a normalization procedure for variations in Mn content by using ratios such as Zn/Mn, Zn/(Mn+Fe) and Zn/Co. (Co is scavenged most by Mn and if a constant, low background prevails, the Co levels will reflect intensity of scavenging). He also states that Pb is scavenged by Fe rather than Mn (this is known to be the case for As), and proposes the use of Pb/Fe ratios of the pebble leach solutions.

Barium is also scavenged by Mn oxides, the secondary mineral hollandite (occurs in the Dundas area) being a natural example.

Whitney (1975) noted some ambiguous relationships for Pb, with a tendency to follow Mn in those samples with high Pb concentrations, and Fe in samples with lower Pb values.

In the joint venture areas, Mn availability is not necessarily related to mineralization. Metal ratios to Mn and (Mn + Fe) have been intensively studied by the author in the orientation data, and, whilst showing up obvious anomalies, there are some ambiguities in detail. This is similar to the findings of Wagner et al (1978), who disagree with the ratio procedure proposed by Carpenter. They found that clasts of (excess) Mn ore in stream sediments would lower the base metal/Mn ratio, and that where abundant Mn is present, a high Mn and base metal content should be considered as indicators of mineralization rather than high base metal/Mn ratios.

These reports are in accordance with this West Coast orientation data, in that relative values of Cu, Pb, Zn and Mn in pebble coating leaches provide the most obvious and practical guide to mineralization, rather than ratios.

Consistent sample weight/volume relationships and leaching times must be maintained, however.

5) Routine survey usage.

Therefore, for routine survey application, hydroxylamine leach with routine analysis for Cu,Pb,Zn and also Mn, Fe, Co is proposed. Initially, the data for (Cu) Pb, Zn only should be plotted and obvious anomalies determined by inspection.

If results are stored on a computer data bank, it becomes a simple matter to try ratios (or combinations) to Mn, Fe and Co if desired, for re-interpretation.

Splits of the samples should be retained for any follow-up work, such as analysis of anomalous (Cu) Pb, Zn samples by acid leach for Ba, Ag and As. (on uncrushed pebbles).

Sampling density can be at least halved, relative to equivalent stream sediment surveys. More information on optimum sample density will be forthcoming after orientation along Itat Ck. (Beatrice prospect) is carried out.

In the initial stages of exploration, whilst the technique is still relatively new, conventional -80# stream sediment samples should also be collected at each pebble sample site, and results kept under review. Conventional samples are still needed if lithologic variations are to be "mapped" by multi-element geochemistry, although sampling density need not be as close.

All pertinent data on stream parameters, drainage lithologies etc. described under -80# stream sediment surveys should be recorded, and the data treated in the same fashion. Follow-up of anomalies is also as for stream sediments.

II. 4. Reconnaissance Soil Sampling.

Reconnaissance soil sampling is particularly useful in areas of high potential where a drainage network to permit reasonable coverage is lacking.

1) Litter sampling.

There is ample evidence that sampling of the organic surface litter (a form of recycled and homogenized vegetation sample) will reflect anomalous sub-soil values. Such evidence includes

a) the work of Farrell and Orr (1977) in Western Tasmania.

b) Thesis work by Russell (1976) at W. Hercules.

c) numerous overseas publications, plus the author's own experience, in similar soil types elsewhere.

d) earlier work by EZ (in conjunction with mercury analysis, which was spurious due to analytical interferences) over the Mackintosh (Que River) prospect.

e) results of orientation sampling carried out at W. Hercules and the Mt. Lyell areas by N.J. Marshall.

If any further litter sample orientation is desired over a known, strongly mineralized area, this could be carried out on lines 11500 N (anomalous) versus 10700 N (background) of the Rosebery Mine Grid. Line 11500 N gave good C horizon anomalies with supporting I P results.

The litter samples should be sieved free of mineral grains (or washed), dried at 120°c, pulverized and then analyzed by a wet ash ($HClO_4/HNO_3$) procedure for Cu, Pb, Zn, Mn.

Anomalous samples should also be checked for Ba and As in the same sample solution.
Litter samples are highly enriched in base metals, particularly Pb, relative to underlying soils, and must be consistently collected and compared only among themselves.

Litter samples(best developed in rain forest) provide a near-ubiquitous sampling medium in this environment, whereas soil profiles show a tremendous variation from place to place. Thus B or C horizon samples are not consistently available (or obtained by field assistants) in a regional survey, and, besides being more time-consuming to obtain by augering, are a source of high potential sample variability.

In areas where litter samples are poorly developed, such as bare rocky slopes, A_0 humus samples can be substituted, and also analyzed by a wet ash procedure. The change in sample type should be noted,however.

As illustrated by the Basin Lake orientation, care must be taken with A_0 samples to ensure consistency in the amount of (variable) barren quartz grains relative to active organic component. Otherwise false anomalies may result.

As with conventional soil sampling, gross changes in litter type must be noted - eg.) on line 800 W in the W. Hercules orientation, where thick rain-forest litter changes to thin ti-tree scrub litter on the higher, bare rocky slopes.

Reconnaissance litter sampling should be carried out on lines (which need not be cut), along breaks of slope; that is, above creek banks and parallel to contours.

A sample spacing of 50 meters along lines is suggested, with each site marked by flagging tape. Parallel lines should be placed from valley to top of each ridge, preferably along breaks in slope picked out from contour maps or stereo air photos.

The W. Hercules orientation data (hydromorphic anomaly in litter) suggests that spacing between lines of 200 meters should be adequate to detect this mineralization.

2) Detection of hydromorphic anomalies.

The objective of this sampling is to detect residual and/or hydromorphic (downslope displaced anomalies. Thus displaced anomalies can be detected in litter over glacial overburden. Such anomalies may find their way into streams by groundwater movement, and therefore this phase of sampling is a logical follow-up to detection of stream sediment anomalies - particularly pebble coated ones in glaciated areas.

Any terraced peat deposits or bogs should be sampled and parallel (contour) lines should be sampled above these. (Such micro-environments can act as a trap to prevent further dispersion down-slope).

3) Wad and talus sampling.

In addition, -80# samples and any Mn wad deposits should be collected from the base of any talus slopes, as these are also loci for the emergence of break-in-slope hydromorphic anomalies.

Such reconnaissance soil sampling would be particularly rapid and cost-effective if only a minimum of scrub cutting is done, and the suggested field positioning equipment (Appendix B) proves to be practical.

5. Reconnaissance Rock Sampling.

1) Wall-rock alteration and ore/gangue associated elements.

Sampling for Cu,Pb, Zn, Mn, Fe, carbonate, and the alteration elements K, Na, Rb, Ba, Zr, F, B, Ti, is advocated to detect wall-rock alteration and element association of the Rosebery footwall schist type.

There is good evidence from the W. Hercules orientation rock samples that Mn, K/Na ratios, Rb, K/Rb ratios, Ba and F are excellent guides to proximity of ore in the footwall altered host rocks.

All these rocks were reported by Beevers (pers. comm.) to be "highly reactive" with acid, due to abundant carbonate.

In the field, carbonate presence and relative abundance can be measured and logged on a relative basis by use of acid. Relative K content can be estimated by using a portable gamma spectrometer (K^{40} channel).

Tourmaline, sphene, fluorite and barite are known gangue minerals at Rosebery, (Braithwaite, 1969). Barium also occurs in altered wallrocks as a Ba rich muscovite mica (Gee, 1970), where Ba substitutes for K, as well as occurring as barite in gangue and in a zoned barite orebody.

Hence B, Ti, F and Ba are potential guides to favourable host rocks.

Unfortunately, much of the detailed thesis work on Rosebery and environs concentrated on traditional silicate analysis and a few trace elements amenable to simple atomic absorption determination. These are not very diagnostic in view of the environment of rapid volcanic/pyroclastic deposition.

The more diagnostic elements such as Ba, B, F, As, Rb tend to have been overlooked, whereas major silicate elements are by definition confined to narrow compositional variations within an acid volcanic environment. Attempts by several theses authors to solve classification using sophisticated methods such as multivariate factor analysis were unsuccessful because the variables chosen (eg. SiO_2) had little diagnostic power and the data formed a closed array (added to 100%).

In this report, alteration rock studies have been suggested on Mt. Lyell ground in the White Spur and Beatrice grid areas, to define "more favourable" sub-areas within Cu-Pb-Zn anomalous zones.

If further orientation work is desired on rock alteration elements, the Rosebery mine grid, lines 11500 N and 10700 N may provide a suitable case history.

2) Routine analyses recommended.

The most cost-effective approach to alteration rock analysis is:

a) Emission spectroscopy scan for B, Ba, Ti, Zr.

b) Follow-up of anomalous Ba by XRF (more accurate).

c) HF/aqua regia digest and atomic absorption for K, Na, Rb, Mn, Fe, Cu, Pb, Zn.

d) As from above solution by hydride evolution (if base metals are low - these interfere by suppressing As evolution) or colorimetry, using digest solution c).

e) F by NaOH fusion and selective ion electrode.

f) The analyst should be requested to note carbonate reactive samples. Quantitative carbonate analysis can be done by Leco induction furnace and weighing of evolved CO_2.

6. "Plumbing System Samples."

These are also a useful guide to proximity of blind mineralization, particularly in glacial covered terrain.

These consist of Fe, Fe/Mn and Mn (wad) secondary oxides developed in fault planes, joints, and shear zones in rocks. They also occur on exposed seepages in creek banks and glacials, and as recent material cementing rock scree.

These should be collected and analyzed by an acid dissolution procedure for Cu, Pb, Zn, Mn, Fe, Co, Ba (by AAS). Anomalous samples should also be checked for Ag and As. The Co values are a guide to relative enrichment by scavenging, as Co is a low background element in this terrain. Any anomalous base metal values are likely to be valid unless Co is highly enriched (50-100 ppm) in the sample. Orientation studies have shown that this is not the case, and "scavenging" to produce false anomalies is not as great a problem as previously assumed. In fact secondary Mn oxides are a valuable sampling medium in this environment.

7. Detailed Rock Samples.

These should be collected from drill core, costeans and outcrops encountered during follow-up grid survey.

The usual rock alteration elements discussed previously should be determined, at least at fairly regular intervals to give sufficient samples (say 10-20) from each costean, drill section or grid area to help classify associated Cu Pb Zn mineralization. The base metals Cu, Pb, Zn and Mn should also be determined, along with Ag and As.

Total sulfur values (by Leco induction furnace and iodimetric titration) may also be useful.

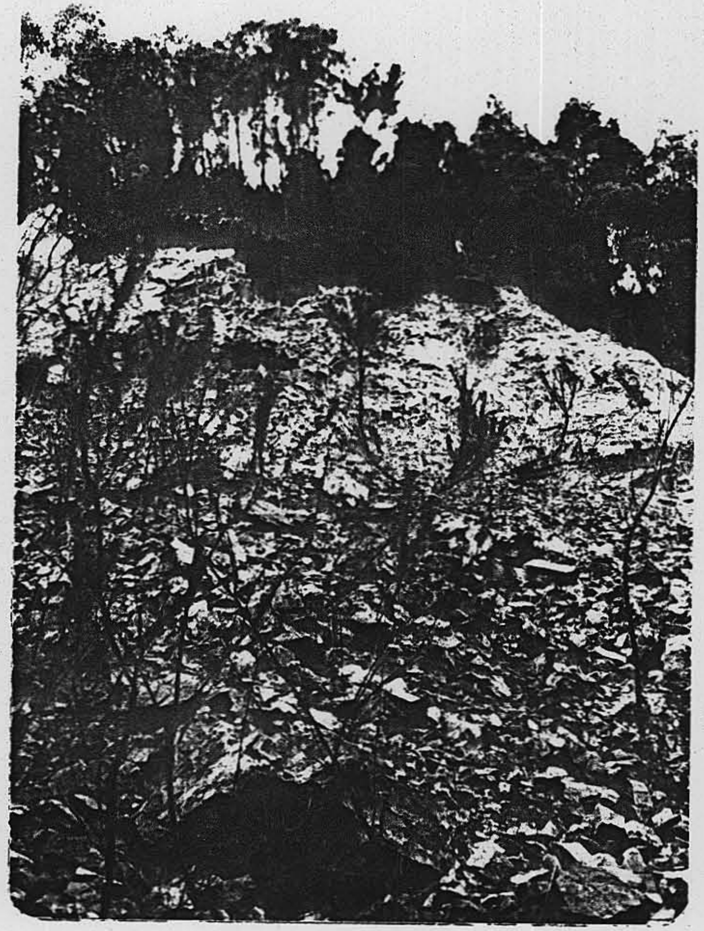
All drill core should be logged with acid for carbonate content, and thin and polished sections made where appropriate.

In sampling drill core, a core shaving device such as that built for CRA Exploration Pty. Ltd., by the EBR railway workshops in Burnie may prove useful.

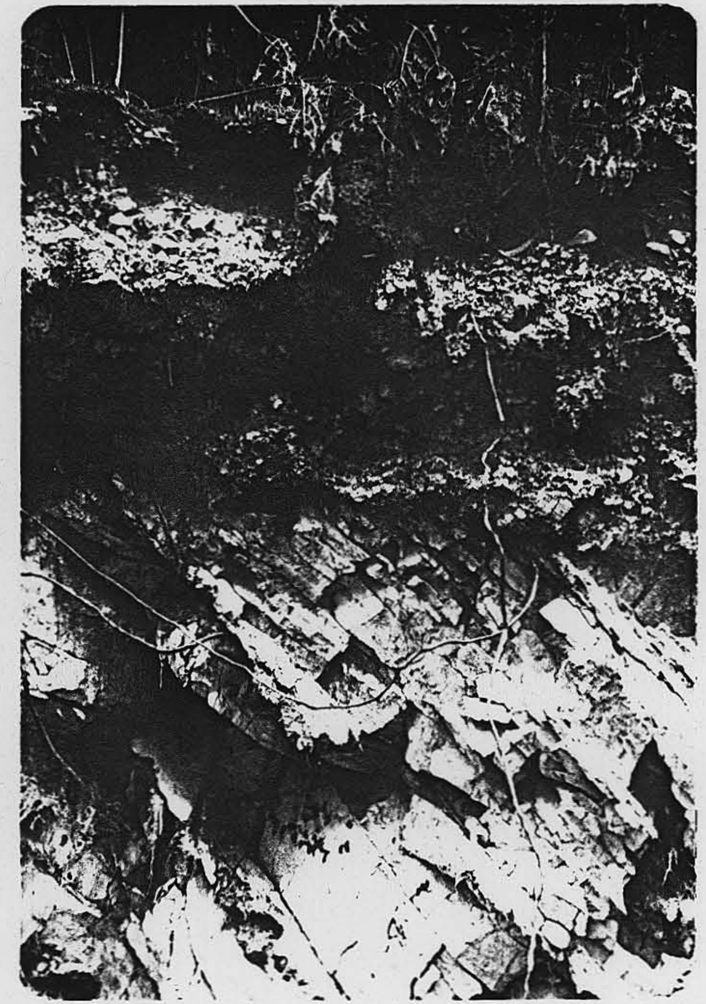
Representative sections of drill core host rock lithologies should be sampled in addition to mineralized sections, and analyzed for base metals, Mn and alteration element assemblages. In this way, a case history file will evolve which will enable more confidence to be placed on future classification procedures.

If the data are recorded on a computerized data bank, it can be readily updated with future information such as extra analyses (all samples must be retained). Any sophisticated multivariate classification procedures can be readily tried at any stage once the data are in this accessible form.

"Plumbing system"sampling is also applicable at this detailed scale.



II. 1. Queenstown - Strahan Road.
Litter (A_{00}) overlies thin A_0 and A_1 on bedrock siltstones.
Juvenile soil -stony lithosol.

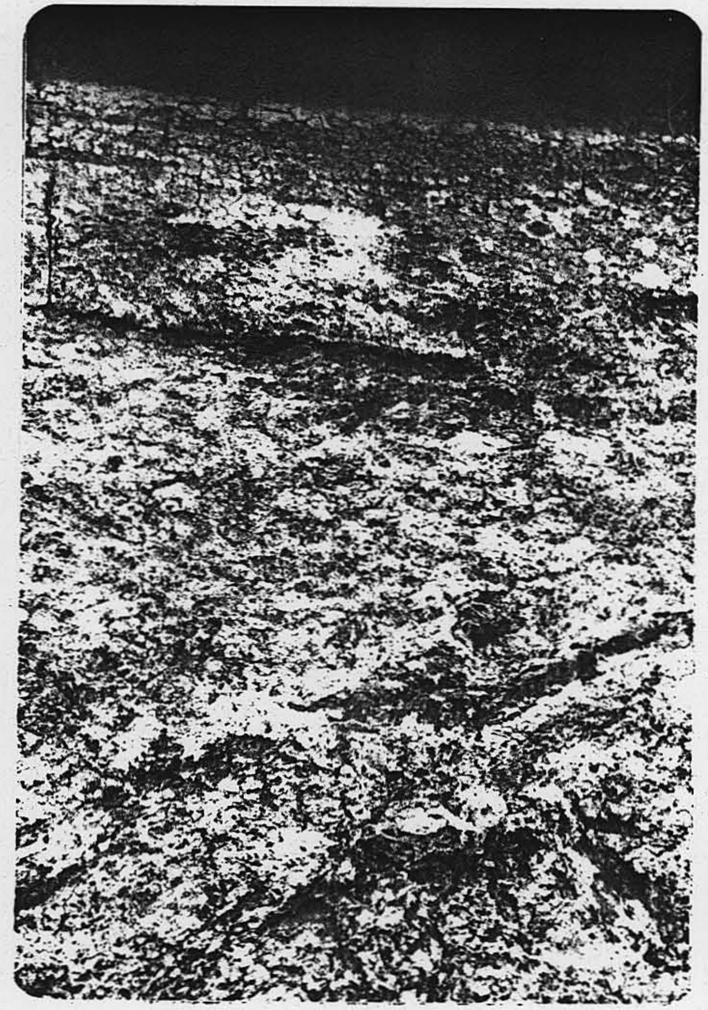


II.2. Queenstown - Strahan Road.
Closeup near II.1.
Stony lithosol (skeletal mountain talus soil), juvenile, with poor profile development (azonal) except for overlying A_0.

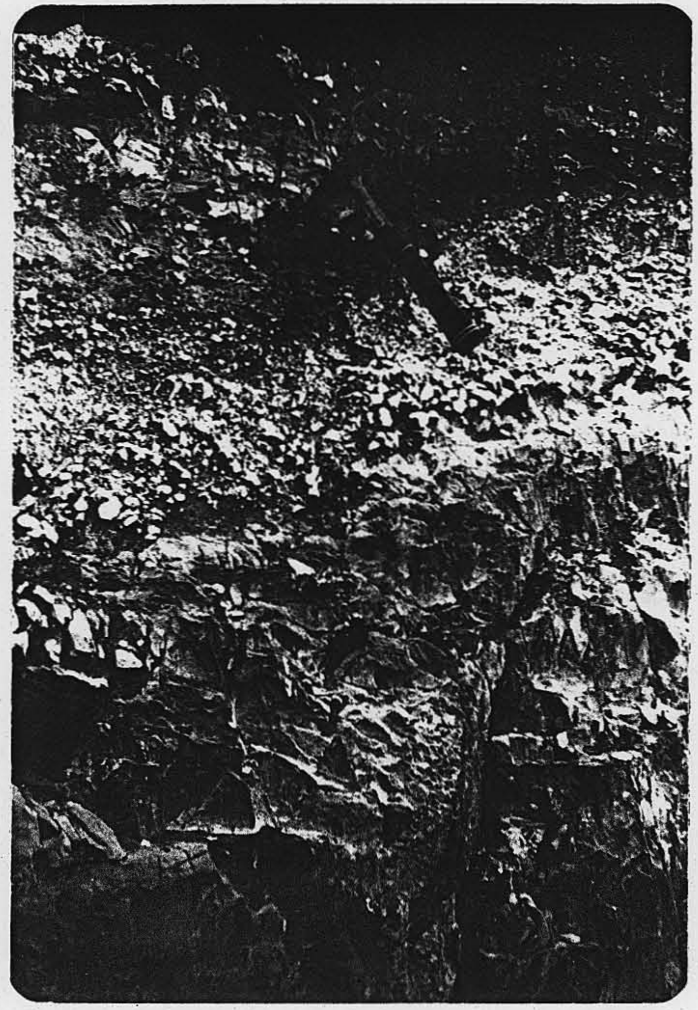
II.3. Queenstown - Strahan Road. (halfway) Thick peaty, wet soil A_0 horizon under cutting grass (swampy), overlies slightly bleached A_1 organic soil at hammer point. Soil is juvenile and sits directly on bedrock siltstones.

II.4. Queenstown - Strahan Road near Strahan. 50 m E of 2/7. A_0 A_1 soil on B horizon over partly consolidat C horizon parent glacials. B horizo development is very localized in this area.

II.5. Glacial soil profile, Beatrice drill site access road. Parent boulder clay overlain by leached A_2 horizon with thin cover of litter.



II.6. Relict placosol podzolic soil
Queenstown -Strahan Road, near Strahan. $A_0$and A_1 dark humus soils overlying leached A_2 horizon on C horizon boulder clay (glacial) grading into less weathered parent glacial (D horizon) at depth. Incipient B horizon development below A_2. Dark band is placon of Fe/Mn oxides.



II.7. 3 km. W of Queenstown.
Complex example of localized fossil soil horizons due to scour and fill. Bedrock is black shale, leached toward top (incipient C horizon development). Overlain by layer of transported quartz rubble filling depressions in bedrock surface. Overlain by strong A_0 soil poorly differentiated into a lower A_1 zone.

Hammer point - overlain by weathered, Transported shale rubble, which in turn is overlain near surface by A_0 poorly differentiated into a lower A_1 zone.

II.8. 6.0 km. S of Zeehan junction, on Queenstown highway. Highly weathered sediments (C horizon) with large patches of Mn wad (on right - sample 24537). note A_0 horizon and lack of B horizon.

II. 9. Henty River - note tannic and humic acids producing deep brown color.

II. 8. Detailed Soil Grids.

These are carried out at the penultimate stage of follow-up, (prior to costeaning) on geophysical anomalies, and/or follow-up of more widespread geochemical sampling as previously described.

II.8.1. Barren sulfide responses.

Where soil sampling over prominent I P responses fails to produce well defined anomalous zones in base metals, it must first be ascertained by examination of soil profiles that the sample medium is valid for reflecting any bedrock mineralization. ie.) thick glacials, or placosol soils are absent. It may be necessary to dig several pits to ascertain the true nature of the profile.

If the sampling appears valid, then re-analysis of one or two critical lines should be carried out for As, Fe and $SO_4^=$. Anomalous arsenic, iron and soil sulfate, unsupported by base metal anomalies, will help explain any I P responses due to barren pyrite. Relatively anomalous Ni values (for acid volcanic terrain) may relate to pyrrhotite.

2 Soil types.

A great variety of local soil types exists in this complex environment, due to changes in topography, rock type and vegetation. A complicating factor is that these changes can occur several times over any one grid, and each change may alter relative background levels and responses to anomalies.

It is imperative to interpretation that these changes be recognized, coded on the recommended computer data bank forms, and mapped. Digging of pits over several sub-areas of a grid may be necessary, as reliance on hand augering can be risky.

Some of the soil profiles are illustrated in the photos accompanying this text report. Further profiles are illustrated in the data sections of the Mt. Lyell and E Z reports in connection with specific orientation surveys in these areas, and reference should be made to these.

The following soil types have been recognized.

II. 8. 2. 1) stony lithosols, or azonal soils.

These juvenile soils are characterized by a lack of profile development, except perhaps for a thin veneer of litter and A_0 humus, overlying a grey, somewhat bleached sandy loam. This is generally thin, rests directly on fresh bedrock, and contains numerous fragments of rock scree.

The Beatrice "Porphyry Hill" area and the upper slopes of the W. Hercules orientation line are typical examples.

Apart from any litter (A_{00}) or A_0 organic horizon which may be developed, sampling of any part of this azonal profile will give equivalent results, and augering is not necessary. "Bedrock chips" obtained by augering are probably largely transported down-slope, as is much of the soil, by solifluction.

Thus soil anomalies should be followed up-slope and backed up with extensive rock sampling of outcrop.

See photos II.1, II. 2.

2) <u>glacial cover and overlying soils.</u>

Valley glaciation gives rise to scour and fill local boulder deposits (usually Owen Conglomerate) in a matrix of water-worn quartz sand and boulder clay. The latter usually makes the soil impervious and water-logged.

The glacial cover may be thick and extensive near the Owen Conglomerate source, as at Basin Lake, or variable and patchy (filling local depressions), as at White Spur and Beatrice.

A variety of soil types can develop on top of the glacials, which, like bedrock, are regarded as "parent material" in soil terminology.

Depending on local conditions and soil maturity, soils developed on glacial cover can range from azonal lithosols (virtually bare, exposed glacials), through moor peats on glacials, (Basin Lake grid, especially N W area; also photo II.3) to a full profile of A and B horizons as in photo II.4

The latter situation appears to be rare, however, and most glacials are overlain by moor peats or azonal, immature soils with a leached A_2 horizon below A_0 and litter - see photo II.5

Fluvioglacial varve deposits also occur (eg. near Howards Anomaly). These are likely to form a barrier to geochemical dispersion, unless thin enough to give a response in any overlying litter or A_0 via vegetation recycling.

(i) Sampling.

Ideally, glacials should be sampled for -200# fine material at the base, just above bedrock, and cold extraction analysis carried out to detect hydromorphic dispersion from bedrock. This is difficult to achieve in practice, although the suggested auger device detailed in the reprint in the Appendix may help.

Panning glacials to detect heavy minerals (galena, sphalerite and barite) may also assist, but this is a more regional technique.

Most glacials are best sampled by using the litter or A_0 fraction. Hence augering is unnecessary unless substantial penetration, almost to bedrock, can be achieved.

(ii) Dispersion mechanisms.

Even where vegetation cannot penetrate glacial cover, as at Basin Lake, there is a possibility that any substantial underlying orebody will set up an electrochemical cell causing metal ions to migrate upward and outward from the deposit, to form a "rabbits ear" double anomaly. (low zone over the deposit). This has been well documented in recent overseas literature. Accompanying electrochemical migration of base metal ions, there will be an increase in other (including major element) ions in the pore fluid, such that soil conductivity readings will increase and also form a "rabbits ear" anomaly. These chemical manifestations of the self potential effect can be detected by taking soil conductivity readings with a simple meter, and by analyzing for cold extractable base metal in the soil.

Any base metal ions in the pore fluid of glacial soils should also be fixed and enriched in the overlying organic horizon.
Unfortunately the Basin Lake orientation failed to give unequivocal evidence of conductivity anomalies or "rabbits ear" metal anomalies, presumably because mineralization is too weak. A response to the altered and weakly mineralized zone was detected, however.

To more definitively test the application of electrochemical migration through glacials, as an exploration technique, orientation over massive mineralization such as at Koonya (E Z mine lease) should be carried out.

Local glaciation as at Beatrice may physically redistribute mineralized bedrock such that it is caught up in the till itself. This would give a surface geochemical response similar to that from mineralized bedrock as parent material. Such situations can be identified (as anomaly follow-up) by panning to look for mineralized boulders in the till.

Hydromorphic anomalies can occur in glacial cover, where ground-waters containing base metal ions flow downslope near the glacial/bedrock interface and emerge at the break in slope.
Frequently, these groundwaters carry Mn which precipitates as Mn wad in seepages in glacials and coprecipitates metal ions. Such "plumbing system sampling" is invaluable as a guide to proximity to mineralization in glacial terrain. (eg. Beatrice, sample 24527, photo II. 1 in Lyell rept. part II).

(iii) Recommended routine approach.

Despite the problems associated with valley glaciation, surface geochemistry does work in a general sense, due to a combination of the discussed factors. The Beatrice grid results are evidence of this, as is the recent publication by Farrell and Orr (1977), and various reports in the overseas literature.

As a routine survey application, sampling of litter or A_0 soils over glacials is recommended. Samples should be collected so as to maintain a *constant proportion of organic component* (see Basin Lake results), or else gross variations in the proportion of organics to inert glacial sand must be allowed for. There is probably no useful purpose to be served by augering into glacial material unless it can be penetrated to the base. The samples should be wet-ashed ($HClO_4$/HNO_3) and analyzed by AAS for Cu, Pb, Zn, Mn, Fe.

In areas where glacial development is sporadic, care must be exercised to recognize and map these. The presence of rounded Owen Conglomerate boulders on surface is a good indicator where exposed profiles are lacking. In doubtful cases, washing the clay from suspected glacials will reveal rounded, poorly sorted quartz fragments.

When routine litter or A_0 sampling is undertaken, sample variability is further reduced. The practice of augering to "B" or "C horizon" has introduced much data variability where sporadic glacial cover occurs.

II. 8.2. 3) <u>Placosol soils.</u> (see photo II. 6)

These probably occur fairly extensively on glacial cover. They are defined as "an accumulation of humified organic material above a leached near-surface mineral soil horizon underlain by an impermeable iron oxide layer"....."The most important feature of placosols is the placon, a thin (1-30 mm) iron oxide layer, that forms 20-150 cm below surface. The placon is essentially impervious to water and effectively divides the soil into two separate hydrologic and chemically dissimilar environments. Due to strongly acid conditions above the placon, base metals are leached from the soil and severely depleted or completely absent in the -80# fraction. Below the placon, chemical conditions are reducing and neutral to slightly basic; metals are relatively stable and distribution patterns reflect those existing before placon development". (Tilsley, 1977).

Placosols form under cool, abundant rainfall conditions where pre-existing soils (particularly glacial boulder clays) become water saturated. This generally occurs downslope from freely drained soils. Humic acids from the overlying vevetation will leach metals downward from the underlying soil to form a bleached A_2 zone, (podzolic soil development) and precipitate an impermeable limonite layer (placon).

This prevents drainage and promotes water-logged soil, anaerobic conditions and development of peat.

The soil below the placon may be relatively dry. Blanket peats, "perched ponds" on glacial deposits and perched water tables are usually the result of an underlying impervious placon.

Placon development is a transient condition in immature soils, and Tasmanian situations are probably relict placons, which can be localized and sporadic. These would give rise to a low geochemical response occurring as a "window" of low background in a soil survey.

(i) Chemical dispersion - distribution of anomalies.

Below the placon, groundwater movement downslope can take place, and hydromorphic anomalies will develop in streams and at seepages in breaks of slope, as well as where placons are breached (relict placons) by subsequent soil development. The placon is absent at the spring line.

The peat layer may act as a metal collector in such situations, whereas organic or inorganic soil samples collected above relict placons will be ineffective due to metal depletion through leaching, and isolation from any mineralized pore water by the impermeable membrane.

(ii) Recommended follow-up in routine survey.

The practical effect during routine soil surveys is that any anomalous responses must be examined for hydromorphic dispersion below a placon layer. Anomalies in water-logged soil should be followed upslope by depth profile sampling, digging pits if necessary, to recognize any placon layer upslope of the surface anomaly. This layer must then be penetrated to sample the C horizon to locate the source of the anomaly.

II.8. 2. 4) Podzol soils.

These are the normal mostly residual soils which are well developed at Howards Anomaly, Henty River, White Spur, Beatrice and the lower slopes of W.Hercules. They can, however, also develop on glacial material (see photo

In a local sense, the soils may be somewhat transported downslope by solifluction.

Hydromorphic displacement of anomalies for large distances downslope, as at W. Hercules, can be a problem.

Thus any anomalies must be followed upslope to their source by sampling to bedrock.

Podzols are defined as leached soils with good profile development, and form in wet, temperate to cold climates. They are characterized by an A_1 organic rich soil layer (often overlain by A_0 humus and A_{00} litter), underlain by a generally thin bleached A_2 horizon of sandy loam, which in turn is underlain by a red-brown or yellow (or mottled) clay rich layer - the B horizon. This is underlain by C horizon weathered rock and D horizon bedrock. Not all layers may be obvious in any one profile, however.

Humic acid rich solutions and high rainfall cause a downward leaching from the organic layers (A_0 and A_1), and strongly leach the A_2 layer, which is the zone of maximum eluviation of clay, iron oxide and organic matter.

(i) A_2 horizon - avoid sampling.

The A_2 layer is easily recognized as a light colored (off white to pale grey) sandy horizon.
Sampling of A_2 must be avoided at all costs, as negative responses may result. Sampling crews must learn to recognize this horizon so that it is not inadvertently sampled during a routine survey.

(ii) B horizon sampling.

The B horizon is the zone of maximum accumulation of clay minerals and iron oxides, and is characterized by a reddish color and prismatic or blocky structure. In poorly drained, water-logged soils, anaerobic conditions prevail and the normally red ferric clay may take the form of greenish ferrous clay. To assist soil sampling crews in recognizing these profiles, small plastic vials containing <u>undried</u> whole soils should be carried for reference.

The top of the B horizon provides the ideal sample medium for geochemical surveys, and is preferable to C horizon rock samples as it gives an elevated response, is easier to collect, and is easier to prepare. Drying and sieving to -80#, with analysis by AAS from a simple acid digest is all that is required to give excellent results.

(iii) C horizon sampling.

Bedrock samples, where comparatively unweathered, (strictly D horizon) tend to give a very erratic and spotty distribution of metals due to their extremely localized influence relative to soil. In a disseminated mineralization environment, base metal C horizon responses can be erratic due to presence and absence of stringers of sulfide. Alteration element responses will be more uniform, however. C horizon sampling for base metals therefore requires closer spacing than equivalent B, A, or A_0 sampling.

Thus C horizon sampling for base metals (as opposed to "alteration elements" and Mn) is only recommended at the final follow-up stage, such as examining soil anomaly sources upslope for hydromorphic displacement, or narrowing down residual soil anomalies.

(iv) Recommended routine soil sampling.

Orientation sampling, as well as extensive documentation, has demonstrated that sampling A_{00} (litter), A_0 or A_1 organic soils can give equivalent survey results to B horizon sampling. Background levels may be elevated,and not as uniform, due to organic enrichment, and contrast may not be as great, however, as in B horizon soils.

However, unless B horizon can be consistently and readily sampled in practice (as at Henty River Grid), sampling of the organic rich surface horizons may be preferable.

(v) Types of podzols in this area.

In the areas studied, true podzols, grey brown podzolic soils, yellow podzolic soils and gley podzols (groundwater podzols) have been recognized.

True podzols have a highly leached, whitish A_2 horizon with little dark A_1 development.

Grey-brown podzolic soils are less severely leached,occur in warmer microclimates, and have a thin, dark A_1 horizon and a greyish-brown leached A_2 horizon. They are commonly developed on glacial soils in the region.

Yellow podzolic soils occur in the more humid rain-forest on well drained slopes, and are characterized by yellow, limonitic B horizon. Henty River grid is a good example.

Groundwater podzols are water-logged soils with a peaty layer and predominately reducing conditions. Thus the B horizon is a greenish or bluish-grey color due to Fe^{2+}, although seasonal wetting and drying may cause mottling of ferric iron oxides to develop.

II. 8. 3. Summary Statement.

The soil variation in this area is quite complicated and can vary locally in any one grid area.

Every attempt should be made by examination of profiles, digging pits where necessary, to recognize, code and map soil variations, and particularly the occurrence of glacial cover.

Field crews should be instructed to recognize these variations if possible. Standard reference vials of whole, undried soil profiles may assist.

In areas where B horizon is readily and consistently available, this should be sampled in preference to C horizon.

In more complex areas, sampling of litter, A_0 or A_1 (consistently!) will generally suffice, and has the advantage over augering in speed and reliability. B horizon sampling, using augers, should be done where possible as follow-up of anomalous zones.

C horizon (weathered bedrock) and fresh bedrock sampling (D horizon) is recommended where practicable, at the final follow-up stage, for delimiting broader A or B anomalous zones, and defining the source of hydromorphic soil anomalies.

A_2 horizon sampling must be avoided.

II.9. Hydromorphic Anomalies in Soils.

As discussed in the previous section, hydromorphic anomalies in soils (as at West Hercules, where displacement from source is 300 meters) are likely to develop, particularly on steep slopes or where complex conditions (placosols) or thick glacial cover prevails.

1) Recognition.

Hydromorphic anomalies can be recognized by:

(1) Their distribution and relation to topography. (breaks in slope).

(2) Their pattern - dispersion tends to be fan-shaped, becoming weaker and wider downslope.

(3) A Cx/total (1 N HCl versus $HClO_4/HNO_3$) ratio approaching 1.0. This is only applicable for loosely bonded metals in B horizon soils, as metals in organic rich soils are more strongly bonded and clastic components tend to be absent.

(4) Values along the zone will tend to be more uniform (low variance) than residual values near the source, due to the effect of the homogeneous solution front.

(5) There may be an association with Mn wad formation.

(6) Displacement downslope from I P anomalies.

(7) Soil conductivities and cold extractable soil metals may give an asymmetric (downslope)"rabbits ear" anomaly where electrochemical dispersion prevails.

(8) Hydromorphic anomalies will tend to be highest in the finer fractions, whereas residual anomalies are more uniform in all size fractions.

(9) Hydromorphic anomalies in B horizon soils will be greater for mobile elements in the fine fraction but resistates such as Ba, Sn, B and Ti will favor coarser fractions further uphill.

(10) Metal ratios characteristic of ore will differ when fractionation occurs due to secondary processes. Fractionation will increase with distance travelled.

2) Tracing hydromorphic anomalies to source.

The following procedures are suggested for tracing hydromorphic anomalies at their source.

(1) Use any upslope geophysical response as a guide.

(2) Use any favourable mapped contacts or tectonic features upslope as a geological guide.

(3) Carry out sampling to bedrock or take outcrop samples where possible on one or two lines across the anomaly. Analyze for base metals and alteration assemblage metals and follow up-slope.
For example, the W. Hercules orientation demonstrates that the major hydromorphic soil (in B horizon and litter) base metal anomaly is unrelated to bedrock source. The bedrock source, although low in base metals throughout, (one minor exception) shows systematic decrease in Fe, and increase in Mn, carbonate, Ba, Rb, F and K/Na ratio as the orebody source is approached. This effect persists well beyond anomalous Cu Pb Zn bedrock.

(4) Sample soil profiles systematically with depth and follow-uphill on one or two lines across the strike of the anomaly. Within any one soil horizon, values will increase with depth as the residual source is approached.

(5) In the immediate proximity to ore, bedrock sampling will reveal base metal mineralization, as can soil sampling. This is more localized than the alteration assemblage effect discussed in (3) above.

(6) If two parallel anomalous soil zones occur, the uphill one may represent residual anomalies in underlying bedrock, and the downhill one the same anomaly displaced hydromorphically.

II. 10. Data Recording and Plotting.

All samples collected routinely should be coded and filed in a computerized data bank, with relevant parameters such as lithologies, soil type, downslope direction and grid coordinates. Coordinates should preferably be the Australian Metric Grid, or alternatively some large local grid system referenced to a remote south-west origin. (all lines are eastings and northings only). Sub-grids, local use of shifting base line references, references to west and south directions etc. should be avoided as these can lead to confusion with machine plotting.

1) Digitizing coordinates.

Old grids, those where sample lines are not ideal, and stream sediment surveys can be coded to a universal grid reference system for subsequent machine plotting with an on-line computer and digitizing table.

In the case of stream sediments, digitizing is readily done from a simplified drainage map showing sample numbers.

Soil grids with irregular lines can be digitized at the ends of each line and at any points of inflexion; thence true intermediate sample grid references calculated and plotted by computer.

2) Computer Forms.

Suitable computer compatible combined field and lab. sheets for all routine soil, rock and stream sediment surveys in this area will be prepared separately, at the local request of the joint venture operators.

3) Sample submission requests.

A simple multiple choice format should also be designed for sample submission to the laboratory, specifying analyses and methods requested.

4) Plotting and interpreting stream sediment and pebble leach data.

Initial interpretation of stream data would consist of data bank listings, and hand drawn, colored "worm diagrams" on simplified drainage base overlays (at geological or photogeological map scale). Separate transparent base overlays to the photogeologic map base should be used for Cu, Pb and Zn, using some arbitrary color code for these worm diagrams, such as red, yellow, green for "strong", "moderate" and "weak" anomalies, with values plotted against each location.

Machine plotting of raw data is convenient on separate overlays. Further interpretation from the data bank would involve automatic sorting of geochemical values related to various drainage basins and lithologies, with plotting of histograms and simple statistical parameters.

Final interpretation may invoke more complex multivariate statistical processing such as plotting ratios, linear regression to correct for varying Fe and Mn contents and stream rank, factor analysis to "map" lithologic variations, etc.
All this is easily and cheaply accomplished, relative to the cost of sample collection, once a suitable data bank is devised.

5) Plotting and interpreting soil grid data.

Initial interpretation of soil grid data is best done by machine plotting (using corrected, digitized grid references) separate Cu, Pb, Zn and Mn stacked profile maps on mylar overlays to the geologic base map and topographic map.

Plotting of actual raw data values is not recommended as this is of no use for pattern recognition, and raw values can be referred to on the data listings. Machine wise this is difficult and expensive.

Contouring is also not recommended, as it invokes the use of arbitrary threshold values which may distort the pattern due to changing backgrounds and geochemical responses. This is particularly a problem over large grids with complex lithology and variation in soil type. Machine contouring can also be relatively expensive.

Stacked profiles, either as line profiles or, preferably, small vertical bars along each line at each sample point, are recommended.

These have the advantage that patterns such as anomalous zones and lithologic changes can be readily seen and mapped from line to line, despite shifting background levels.

A major advantage in complex areas is that anomalous patterns can be seen through background variations (unlike contour maps), and sample variability effects are minimized.

Moreover, the dimension of data variance is introduced, which is difficult to assess on a large sheet of raw number values, and is artificially smoothed out in machine contouring.

Further interpretation such as examination of element ratio plots merely involves the cost of machine plotting another stacked profile map; a task which one would hesitate to try by manual methods.

Such machine plotting is rapidly and cheaply accomplished at rates competitive or cheaper than tedious manual drafting.

6) Progress Maps.

During a lengthy survey, individual lines can be machine plotted on paper strips on a regular turn-around basis. These can be pasted onto a base sheet to provide an up-to-date progress map.

III. DEFINITION OF GEOCHEMICAL ANOMALIES - discussion of pattern recognition.

These have often been defined as values in excess of mean + 2 standard deviations, the data having first been converted to logarithmic values (or plotted on cumulative log-probability paper). Trace element data often appears log-normally distributed; however there is no a priori reason why this should be so, and other distributions such as the gamma distribution may give a closer fit, but are difficult to manipulate. Also, an appearance of log-normality can be due to artificially truncated data where values have a lower cut-off due to analytical detection limit. Overlapping populations due to geochemical dispersion processes can distort log-normal data toward a more normal distribution (Central Limit theorem).

For example, in the Lake Beatrice annual report, Hutton defined thresholds as values in excess of 100 ppm for Cu and Zn, and 300 ppm for Pb, on the basis of cumulative log-probability plots.

However, the cumulative percent frequency graphs for Pb and Zn show a complex structure due to overlapping populations, which is due to the various rock types covered, plus the extra complication of changes in soil type (stony lithosols over the quartz-feldspar porphyry, mature soils in the valley).

There is also the local presence or absence of glacials, and whether sampling was of A_0 , A_1, or B horizon (depending on profile development and the ability of the auger to penetrate).

Hence this "global" statistical approach is not advocated where this type of problem occurs.

Hanson (1977, "fig 6" series) plotted cumulative plots for Cu,Pb and Zn on the Boco grid. The Pb and Zn plots show several straight line segments indicating a series of non-overlapping, well separated log-normal populations.

Overlapping populations can be sorted out and threshold values assigned to each, using the methods of Sinclair (1976) .

Figs 7a and 7b are frequency/probability plots for Pb on the Lake Beatrice Grid, on lines 14 N to 20 N, (predominately residual soils) and lines 8 N to 12 N (predominately over glacials - M.J. Hutton, pers. comm. N.B. glacials not shown on map for sampled portions of these lines).

These plots were also done without prior separation of rock type, and several overlapping populations can be seen.

Population A is clearly defined in both figures, whereas B,C (and D) have a large amount of overlap. In fact on fig. 7a, populations B,C and D, although probably real, are contained within the 95% confidence belt as defined by Lepeltier, (1969), so can to a first approximation be treated as one.

In plotting figs 7a and 7b the recommended practice of assigning about 15 equal (log-normal) class intervals throughout the range has been followed, (after disregarding a few extreme high values) with cumulation from highest to lowest value. This avoids losing the important anomalous values through inability to plot them on probability paper.

Many such graphs can be drawn, for each element, element ratios, over each rock type, soil type etc.

To do this by hand is very time consuming and was therefore not pursued further - such data manipulation is best done by computerized methods between field seasons.

The definition of anomalies as mean + 2 standard deviations is purely a statistical concept without any necessary significance in the geological sense.

Thus if all samples were taken from the one site, a cumulative curve could be drawn which would show only one population, a steep slope (ie narrow spread of values, small variance due to analytical + sampling errors) and define 2½% of samples as anomalous.

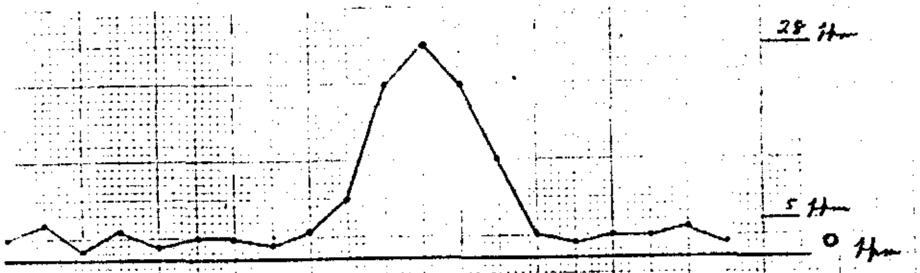
The main use of such graphs is in defining populations (including overlapping ones), which can then be related to lithology changes and mineralization. This can be useful when working in areas of deep cover where geology is inadequately known, or in regional stream sediment work where drainage geology is not well mapped.

Since the Beatrice Grid is over well mapped geology, there is no point in using such graphs to define populations.

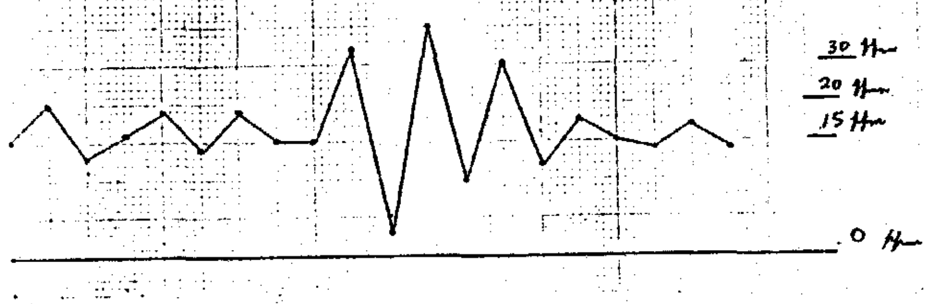
The important point is that geochemical anomalies are best defined by a pattern recognition process, considering all variables (geology, geophysics, structural disturbances, and all elements together) simultaneously.

It is not only what values are high, (eg over 100 ppm) but <u>where</u> they occur on the map, with their spatial relationship to geologic elements and to all other significant geochemical elements.

Another feature which is often not considered by global application of univariate statistics is that anomalies over mineralization tend to have a higher variance, (ie are more "noisy") than those over background areas. This is apart from high values occuring as such. The diagrams below show the effect of signal/noise ratio on anomalies.



idealized anomaly concept of a high zone



variance anomaly concept

In the variance anomaly concept, the anomaly forms a <u>zone</u> of individual high and low peaks, but the highs are not necessarily obvious if taken as numbers in isolation from their surroundings.

Similarly, metal ratios may be highly correlated over one rock type (eg Pb/Mn in altered tuffs at Beatrice) and not correlated over another (eg Pb/Mn over quartz-feldspar porphyry at Beatrice - see plots for line 16 N; figs. 10a,10b,11a,11b).

A global statistical approach could distort this Pb/Mn correlation depending on the relative proportions of samples taken over each rock type.

Hence in the first instance, stacked line profile plots at map scale are advocated as a pattern recognition process. A separate map should be prepared for each element, and overlays all compared with each other and the geological (and topographic) map base at the same scale to visually recognize anomalous zones and trends.
This is also a fairly time consuming process, and best done by computer plotting once a data management file has been established.

IV. COST ESTIMATES FOR PLOTTING STACKED PROFILES

Discussions were held with Earth Science Computer Corporation, of 556 Princes Highway, Rockdale, NSW. (telephone (02)5972241) on this subject.

This organization is experienced in plotting magnetic profiles, contours, and stratigraphic sections and produce a high quality product at rates which are difficult to match by manual drafting of equivalent quality.

To carry out an initial trial on a small area, such as the N E quadrant of the Mt. Lyell White Spur Grid, which involves about 250 data points for 4 elements (Cu Pb Zn Mn), the cost break-down is:

1) Digitizing.

   Ends of lines and points of inflexion would be digitized from the base map provided, and referred to an arbitrary grid origin such as the S W corner of the map. (unless an AMG grid reference is provided).

   Cost = $30.

2) Program development. (once only charge for this and subsequent work).

   A small program must be developed to calculate grid references for intermediate sample points between the digitized ends of lines and points of inflexion.

   Cost = $50.

3) Punch data onto disc file from result sheets; 250 points for 4 variables.

   For small jobs this is usually sub-contracted out at cost price, which is 14 cents per punch card, including verifying, and the data transferred to disc.

   Cost = $35. (alternatively, these data can be punched at Queenstown or Rosebery.

4) Plotting program development. (once only charge for this and subsequent work).

   A small program will be developed to enable optional line profiles and/or bar profiles to be plotted at a suitable vertical scale. eg.) 1 cm. = 100 ppm. Scales can be changed optionally. Off-scale results, which would cross onto the next line, can be identified by using a system such as one or two arrow-heads at the upper plotting limit to identify relative strengths of off-scale anomalies.

   Cost = $100.

5) Plotting.

It is suggested that initially two elements be plotted as line profiles and two as bar profiles to see which method gives the better presentation.
Cost is $30 per plan (per element) for each small mylar transparency, irrespective of whether line or bar profiles are produced. Thus for $120, 1,000 data points have been accurately drafted.

6) Ratio plots.

Plotting of ratios such as Zn/Mn or (Cu+Pb+Zn)/Mn can be done at no extra cost save the standard $30 per plan. For plotting production sized jobs, such as the entire White Spur Grid (approx. 1,000 sample points), costs are:

1) card punching and verifying at 14 cents per card
$140 - 00

2) digitizing end points and inflexion points on lines, at $2.50 per line for digitizing, plus $1 per line to interpolate intermediate stations.
35 lines at $3.50 per line $122 - 50

3) Plotting profiles on mylar, at $100 per A_0 sheet
Cu Pb Zn Mn $400 - 00

total $662 - 50

4) Ratio plots - at $100 per sheet.

This is a comparatively small outlay for the interpretation of 4000 data values, considering the collection and analysis costs of the 1000 samples involved.

Costs for the E Z Mt. Black sheet 7 would be on a similar basis for plotting, with variations depending on number of cards punched and lines digitized.

V. GENERAL COMMENTS ON MT. LYELL LABORATORY

This laboratory, whose prime function is to serve as a mine assay facility, is adequately staffed and equipped for geochemical exploration work.

There is,however, room for improvement, mainly in organization of sample submission and result sheets, and in the use of simple laboratory aids which could probably double throughput and hence lower costs using the existing staff structure.

A few notes are given below by way of general outline, but it is recommended that a few days consulting with On-the-job training could achieve much. Specific details of various procedures, both for geochemical and mine assay work could then be given, as the latter has been influenced by a largely traditional approach.

It may be worth considering a laboratory service for both joint venture operators, as there are many advantages to be gained in having in-house facilities where a ready base (mine lab.) already exists.

1) sample digestion should be performed in pre-numbered racks of 50. This obviates labelling individual tubes and is a time-saving procedure.

2) at least one efficient, properly engineered (for air flow characteristics) fume cupboard should be purchased for HF work and perchloric digests in the longer term.

3) pre-graduated culture tubes should be used.

4) screw-top culture tubes should be used for shaking procedures.

5) weighing would be much faster if an electronic top-pan balance with automatic taring is used, with a Mettler vibrating spatula for dispensing the sample.

6) Oxford dispensers (or equivalents) should be used for rapid addition of reagents.

7) an automatic diluter would save the time-consuming process of manual dilution or re-calibration of the AA unit using burner rotation, and achieve higher precision.

8) a range of Eppendorf type dispensing pipettes is needed.

9) the AA6 unit should be sent to Deltron Pty. Ltd., 4 French Lane, Summer Hill, N.S.W. (phone (02) 7992022)for complete overhaul.

10) the old AA3 should be reconditioned by the above, and converted from 50 cycle to 256 cycle modulation. It would form a useful back-up during heavy work-load periods.

11) casual labor could be employed for tasks such as weighing, sample digestion and washing glassware.

12) distilled water blanks are sometimes high. The cause should be investigated and rectified - if necessary with a back-up ion exchange unit. Instrument zero should be set on the blank.

13) ultimately, a new AA unit with simultaneous background correction facility is desirable.

14) sample submission forms need to be redesigned to a simple multiple choice format. Thus analytical methods can be quickly specified, and if NCR paper is used, copies are available for the laboratory and the geologist.

15) results should be entered directly onto an 80 column card format on NCR paper (copies for lab. and geologist, and original to data processing centre for entering onto punch card or tape files). Ideally the sample number and details could be pre-coded by the geologist on the left hand section of the form.

16) wet strength Kraft envelopes (large size) with numbers pre-stamped (with a sequential stamping device) are preferable and cheaper to the present system, of calico bags for soil and stream sediment samples. The samples could be dried, sieved and the -80# portions put back in the same (or smaller) envelopes, and the oversize rejected. Each geologist should be responsible for his own set of numbers, for which he keeps a register book. Rock sample "ticket books" are not as convenient.

17) a card-index file of area, line no., sample numbers included, elements analyzed, date, method etc. should be instituted. Such cards would refer to each standard size box containing prepared samples in packets. All boxes should be given an index no. referred to on the cards and analysis sheets, and stored in number sequence on Dexion shelves.

18) the large jaw crusher used for rock samples in the mine preparation area is difficult to clean out to reduce contamination for geochemical work. This problem is recognized and blanks are run, but the sequence of cleaning, crushing, splitting, fine crushing and pulverizing is time consuming and unnecessary for geochemical purposes. The present throughput of 5 samples per hour for 2 people is far too slow - 15-20 per hour should be attainable. Ideally, a 4 inch jaw crusher should be set up in a separate area for geochemical samples. Samples can be reduced in this directly to -0.1 inch, then a mixed grab sample pulverized for 3 minutes in a swing mill using 100 ml capacity vessels.

Splitting of samples increases the risk of contamination, and is very labor intensive and unnecessary for geochemical studies.
Suitable equipment can be purchased from Rocklabs of Auckland, New Zealand, at very competitive prices.

19) a laboratory vortex mixer would speed up mixing of sample digests. (presently done manually).

In summary, the latest costs for geochemical analysis (R.M.D. Meares memorandum, 13.3.79) are reasonable, when compared to charges from outside laboratories.

With the added potential advantages of fast turn-around, on-site communication and freight savings, the use of this laboratory for all routine geochemical analyses should be encouraged.

For a comparatively modest outlay, efficiency in sample throughput should enable a profit to be realized against these analytical charges. This can help defray wages and the overheads in extra equipment outlay, particularly if both joint venture companies agree to use the same facility.

BIBLIOGRAPHY

Anderson, W.B. (1972). The Mt. Read volcanics in the Rosebery-Tullah area: petrology, geochemistry and possible tectonic significance. Hons. B.Sc. thesis, Univ. of Tasmania.

Baker, W.E. (1973). The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization. Geochim et Cosmochim. Acta vol. 37 p. 269-281.

Bolviken, B. and Logn, O. (1975). An electrochemical model for element distribution around sulphide bodies. In Elliott, I.L. and Fletcher, W.K. eds. Geochemical Exploration, 1974: 5th International Geochem. Exploration Symposium, Elsevier. p. 631-648.

Braithwaite, R.L. (1969). The goelogy of the Rosebery ore deposit. Ph.D thesis, Univ. of Tasmania.

Burton, C.C.J. (1975). A description and appraisal of exploration work undertaken by Comstaff Pty. Ltd., on E L 5/63. Unpublished report no. 121 for Electrolytic Zinc Exploration.

Carpenter, R.H. and Hayes, W.B. (1978) Precipitation of iron, manganese, zinc and copper on clean, ceramic surfaces in a stream draining a polymetallic sulfide. deposit. J. Geochem. Explor., 9: p. 31-37.

Carpenter, R.H., Robinson, G.D. and Hayes, W.B. (1978). Partitioning of manganese, iron, copper, zinc, lead, cobalt and nickel in black coatings on stream boulders in the vicinity of the Magruder mine, Lincoln Co., Georgia. J. Geochem. Explor., 10: p. 75-89.

Carpenter, R.H., Pope, T.A. and Smith, R.L. (1975). Fe-Mn oxide coatings in stream sediment geochemical surveys. J. Geochem. Explor., 4: p. 349-363.

Chao, T.T. and Theobald, P.K. (1976). The significance of secondary iron and manganese oxides in geochemical exploration. Econ. Geol., Vol. 71, p. 1560-1569.

Dickson, J.A.D. (1965). A modified staining technique for carbonate in thin section. Nature 205 p. 587.

Eastve, C.J. (1973). Geological and geochemical variation in the Rosebery Host Rock Horizon. Hons. B.Sc. thesis, Univ. of Tasmania.

Farrell, B.L. and Orr, D.B. (1977). Prospecting in areas of glacial overburden in Western Tasmania. Proceedings of Aus. I.M.M. Conference, Tasmania, May 1977 p. 93-108.

Fitzgerald, F.G. (1974). The Primrose Pyroclastics in the Hercules-White Spur area, Western Tasmania. Hons. B.Sc. thesis, Univ. of Tasmania.

Gee, C.E. (1970). The geochemistry of some black shales in relation to the origin of certain stratiform orebodies in Tasmania. Ph.D. thesis, Univ. of Tasmania.

Govett, G.J.S. (1973). Differential secondary dispersion in transported soils and post-mineralization rocks: an electrochemical interpretation. In Jones, M.J., ed., Geochemical Exploration 1972: 4th International Geochem. Exploration Symposium, London. Institute of Mining and Metallurgy, p. 81-91.

Hanson, N.H. Report on exploration undertaken in the Bulgobac exploration licence 12/72. E.Z. Co. Geological rept. 128.

Hutton, M.J. Annual Rept. Dora-Huxley, E L 10/69 (1977-78) Mt. Lyell Mining and Railway Co. Ltd., Exploration Division.

Marshall, N.J. (1976) Geochemical reconnaissance stream sediment survey and other geochemical investigations in northeastern Montenegro in 1975. Unpublished report no. 8, project YUG/73/010, United Nations Development Program.

Mears, R.M.D. Annual Rept. Henty-Yolande E L 41/71 (1977-78) Mt. Lyell Mining and Railway Co. Ltd., Exploration Division.

Mill, J.H.A. Bulgobac exploration licence E L 12/72. Progress report on Activity, Oct. 77-78 E.Z. Co. Geological rept. 129.

Rivers, W.M. (1975). The geology and geochemistry of the Tullah area. Hons. B.Sc. thesis, Univ. of Tasmania.

Russell, D.W. (1976). The biogeochemistry and pedogeochemistry of the West Hercules area, Rosebery, Western Tasmania. Hons. B.Sc. thesis, Univ. of Tasmania.

Sinclair, A.J. (1976). Applications of probability graphs in mineral exploration. Association of Exploration Geochemists, special vol. no. 4

Smith, R.N. (1973). Trace element distribution within some stratiform orebodies. Pt.II Hons. B.Sc. thesis, Univ. of Melbourne.

Stevens, A.G. (1974) The geology and mineralization of the Chester-Pinnacles area, W. Tasmania. Hons. B.Sc. thesis, Univ. of Tasmania.

Stone, (1975). Report on West Hercules area. Unpublished report no. 120 for Electrolytic Zinc Exploration.

Sveshnikov, G.B. and Ryss, Y.U. (1964). Electrochemical processes in sulfide deposits and their geochemical significance. Geochemistry International, vol. 2. p. 198-204.

Theobald, P.K., Overstreet, W.C., and Thompson, C.E., (1976). Minor elements in alluvial magnetite from the Inner Piedmont Belt, North and South Carolina. U.S. Geol. Surv. Prof. paper 554-A.

Tilsley, J.E. (1977) Placosols: another problem in exploration geochemistry. J. Geochem. Explor. 7: p. 21-30.

Wagner, G.H., Konig, R.H. and Steele, K.F., (1978). Stream sediment geochemical investigations in Arkansas - comparisons of manganese, zinc, and lead-zinc districts with an unmineralized area. J. Geochem. Explot., 9: p. 63-74.

Walter, A.C.(1977-78). Annual Rept. Mt. Tyndall E L 9/66 Mt. Lyell Mining and Railway Co. Ltd., Exploration Division.

Whitney, P.R. (1975). Relationship of manganese-iron oxides and associated heavy metals to grain size in stream sediments. J. Geochem. Explor. 4: p. 251-263.

Williams, E., Solomon, M., and Green, G.R. (1975). The geological setting of metalliferous ore deposits in Tasmania. In Economic Geology of Australia and Papua New Guinea, vol.1, Metals. Ed.C.L. Knight, Aus.I.M.M. Monograph 5, p. 567-581.

Williams, R.E. (1975). Progress report on exploration of E L 1/62 (Mt. Black) during 1974-75 E.Z. Co. Geological Rept. 124.

Williams, R.E. (1974). Progress report on exploration of E L 1/62 (Mt. Black) during 1973-74 E.Z. Co. Geological Rept. 117.

APPENDICES

APPENDIX A.

FIELD TESTS

1. Introduction.

Colorimetric based field tests, which are simple but only semiquantitative have become somewhat of a lost art since the establishment of central laboratories using instrumental techniques almost 15 years ago.

Nevertheless, in the rugged environment of the West Coast, there is a place for simple semiquantitative tests for follow-up of stream sediment, and base of slope soil anomalies in remote areas. These can help position and define the limits of detailed grid sampling using laboratory procedures.
Moreover, water sampling can be tried in situ at superior sensitivities.

The joint venture companies have an advantage in that both have access to mine laboratories which can supply and prepare reagents for field use.

In this environment, colorimetric tests for Cu, Pb and Zn are of potential interest. The copper test using 2:2 biquinoline is the most reliable, whereas specific Pb and Zn tests require the use of pH control and masking agents such as cyanide (for Pb test - suppresses Cu and Zn) and thiosulfate(for Zn test - suppresses Cu and Pb at this pH).

However, in the interests of simplicity in this difficult terrain only one test, a variant of the Bloom (1955) cold extractable "total heavy metals" test is advocated.

The usual ammoniacal citrate buffer and hydroxylamine extract used by Bloom and others doubles as a weak cold extractant for Cu,Pb and Zn and also suppresses the potential interference from iron by reducing it to the ferrous state where it is complexed by the alkaline citrate. The pH of 8.5 is optimal for simultaneous complexing and solvent extraction of Cu,Pb and Zn with dithizone.

Two problems are anticipated with this approach.

1) this citrate buffer is a very weak cold extractant for loosely bonded (adsorbed) heavy metals. Equilibrium studies by Beevers (pers. comm.) and the author have shown that extraction equilibrium is slow (up to 10 days). Variations in grain size, organic matter content, clay mineralogy etc. cause great variations in the amount of available metal extracted from sample to sample, in the first few seconds of the reaction. Thus anomalies can be "manufactured" by relative differences in extraction rates when not working near equilibrium.

2) humic acids are extracted by alkaline solutions as used in the buffer. These can impart a yellow color to the organic solvent layer, and also cause frothing and emulsification.

Hence the use of HCl prior to buffer addition, is advocated as an extractant to rapidly remove heavy metals and attain equilibrium. Humic acids are precipitated in low pH solutions.

2. Extractable Heavy Metals in Soils and Stream Sediments

operating field instructions.

1) Scoop 0.1 g of wet -80# sample into a Corning 9826 screw top culture tube.
2) Dispense 1 ml of 6M HCl into tube and agitate contents gently for 60 seconds.
3) Dispense 10 ml of buffer solution into tube, and mix contents.
4) Dispense 1 ml of 0.002% dithizone solution in toluene into the tube, fit screw cap and shake thoroughly for 10 seconds, then allow phases to separate.
5) Observe color of top layer; if it is green, blue-green or blue, record results as 0,½, or 1 respectively. If the color is blue-purple or red, titrate in further 1 ml increments of dithizone, shaking gently for a few seconds only, after each addition to mix contents of upper organic layer.
6) Keep adding 1 ml increments until a blue upper layer results, and record results as 2,3,4,,,, etc.

3. Field Apparatus.

1) Scoop for dispensing nominal 0.1 g sample.
Usually, a small hole is drilled in a plastic bar and a dry -80# sieved sample is packed level. Experience has shown that weight reproducibility is better than ± 10%. With wet samples, it may prove more convenient to wet sieve a portion into a plastic beaker, allow the mud component to settle (organic matter will float) and insert a small length of glass tubing of about 5 mm bore into the sediment to a graduation mark, equivalent to about 0.1 g. A piece of 4 mm thick plastic rod or wire (not Cu Pb or Zn) can be inserted as a plunger to dispense the "core" of sample into the reagent tube.

2) 1 ml plastic "Eppendorf" or equivalent ("Repipet", "Finnpipette") dispensing pipettes with disposable tips are used for adding the HCl and dithizone (keep separate).
A 5 ml (adjustable 1-5 ml, set at 5.0) plastic Finnpipette is used for dispensing buffer.
These are available from Laboratory Supplies Pty. Ltd. 48 Sydenham Road, Marrickville N.S.W. phone (02)5196626 and cost approximately $50 each. They are unbreakable and should last indefinitely.

3) plastic bottles for storage of buffer solution and 6M HCl. A plastic container for water may be useful, or stream water can normally be used to wet sieve and rinse out the tubes.

4) Corning cat. 9826 culture tubes, 20x150 mm, with screw tops and teflon liners.

5) Thermos flask for storage of refrigerated dithizone solution.

4. <u>Reagents - prepared in laboratory</u>.

1) 6M HCl; a 50% solution of analytical grade (preferably "low in lead" "Pronalys", "Suprapure" or equivalent) in distilled and de-ionized water.

2) 0.002% dithizone working solution in toluene (reagent grade).
Prepare fresh every day by 50:1 dilution of 0.1% stock solution with toluene. This can be done in the field (if the stock solution is kept cold in a thermos), by using the 1 ml Eppendorf dispenser and a 50 ml measuring cylinder to measure the toluene.

3) 0.1% dithizone stack solution in chloroform.
Dissolve 0.1 g of fresh, purified dithizone in 100 ml chloroform (reagent grade), by shaking vigorously over an extended period. Cover with a layer of 1% ascorbic acid in water, to minimize oxidation, refrigerate, and store in thermos flask. Prepare fresh every 1-2 months.

4) distilled and de-ionized water. Test purity of water used for making buffer solution, by applying the "heavy metals in water" test.

5) buffer solution - 4 liters. (keeps indefinitely).
200 g of ammonium citrate (purest grade available).
32 g of hydroxylamine hydrochloride and 30 g of ascorbic acid are dissolved in about 1 l. of metal-free water in a large beaker.

Dilute to 2 liters, and add a small amount of thymol blue indicator (in alcohol). Add conc. NH_4OH (about 100 ml) until the solution just turns blue, indicating pH = 8.5
Transfer to a large separating funnel, and remove heavy metal impurities by extraction with 20 ml portions of 0.1% dithizone in chloroform (shake for 2 minutes).
If the dithizone turns red, remove the organic phase and repeat extraction until a mixed green color remains, indicating that all metal has reacted and excess reagent remains. Excess dithizone is soluble in basic solutions (orange color) and must now be removed by extracting first with pure chloroform (in which it is more soluble), and finally with portions of carbon tetrachloride until the organic phase (discarded after each extraction) is almost colorless. (The blue color of the indicator will remain in the aqueous phase).
Dilute buffer to a final volume of 4 liters with distilled and deionized water.
(Alternatively, if water of suitable purity cannot be obtained, dilute to 4 liters initially and purify the whole amount with dithizone extraction. Then add about 50 ml of a saturated solution or dispersion of silicon antifoam (eg. Dow Corning) in acetone to the buffer solution.
Store in a polyethylene container which has been thoroughly rinsed in acid, then water.

6) Purification of dithizone.
Dissolve fresh, high purity dithizone (diphenylthiocarbazone (eg. Merck) in hot chloroform to make an almost saturated solution. Filter through fritted glass, place solution in clean (with acid) vacuum desiccator and evaporate under reduced pressure until reduced to about ¼ of original volume. Collect the precipitate in a sintered glass filter crucible, wash with a few small portions of carbon tetrachloride, and dry in air. Store under refrigeration in the dark.
Use this reagent to prepare the stock solution.
If the dithizone is sufficiently free of oxidation products, this purification may not be necessary. Test by extraction of a 0.1% chloroform solution in metal-free water containing a little metal-free NH_4OH (pH 9-10). The green color will be removed and the chloroform phase should be colorless (not yellow).

5. Notes.

1) Silicon antifoam is incorporated in the buffer to minimize emulsion of organic phase from humic acids in the sample.

2) If emulsion problems persist, try alternative solvents such as xylene or methyl isobutyl ketone in lieu of toluene.

(Benzene is often recommended but this emulsifies readily). Add more antifoam (to each sample) if necessary.

3) A lighter-than-water solvent is used for dithizone in the field test, so that sediment particles will settle. If problems are encountered with sediment remaining in the organic phase, try keeping sediment at the bottom of the tube by adding a plug of (acid washed) glass wool after step 3) of operating instructions.

4) Ascorbic acid is incorporated in the buffer to maintain reducing conditions over and above those normally recommended (hydroxylamine only). Otherwise, the abundant MnO_2 present in many Tasmanian samples may cause oxidation of dithizone.

5) Dithizone, when oxidized to diphenyl-thiocarbazone, fades to a yellow color and such solutions are useless. Partial oxidation will give a yellow-green color, different in hue to pure, fresh dithizone solutions. Partially oxidized solutions should be discarded. (to test for partial oxidation, extract with dilute, metal free NH_4OH - the dithizone will go into the aqueous phase, and the solvent should become colorless, not yellow.)

6) Minimize dithizone oxidation by keeping solutions cool (thermos), and away from strong sunlight. Working solutions are prepared fresh, daily by dilution of stock solution.

7) The ammonium citrate will be found to contain appreciable heavy metal impurities - hence the necessity for purification of buffer.

8) The field test is extremely sensitive - for example, shaking the test tube with a thumb over the top will give a positive reaction if coins have been handled! Hence scrupulous cleanliness is necessary - (wash all reagent containers and tubes with dilute acid and then metal free water before use.) However, once in the field, each reaction is "self-cleaning" and thorough washing between tests is not necessary.

9) The colors observed range from pure green of unreacted dithizone (no heavy metals) to red for completely reacted (excess base metals) dithizone. Intermediate metal concentrations produce a mixed green-blue to grey color due to combinations of green and red end-members. Hence "titrate" by incremented additions to a standard mixed color.

10) The test reacts to Zn + Cu + Pb combined, the relative contributions being about 3:2:1.
If desired, independant laboratory calibration using a standard solution of Zn can enable the readings to be expressed as "acid extractable Zn equivalents". However, a relative scale of 0, ½, 1,2,3.... etc. will suffice for field work.

11) Sensitivity can be adjusted upwards or downwards to suit local conditions by varying the amounts of sample, and strength of dithizone solution. This can be determined by experience, or by trial orientation on a known area such as Itat Ck. at Beatrice.

6. Total Heavy Metals in Waters - field operating instructions.

A similar test can be used for Cu + Pb + Zn in stream waters, with sensitivities of about 2 ppb. (.002 ppm) for Zn, and 10 ppb for Pb and Cu, in a 50 ml sample. (ie far below routine atomic absorption sensitivities).

Organic complexes in the West Coast waters may cause some problems with emulsification, however. Precautions must be taken against Zn contamination.

1) 50 ml of water in a 100 ml plastic stoppered measuring cylinder, rinsed at the site.

2) Add 5 ml of buffer solution.

3) Add 2 ml of 0.001% dithizone in toluene, cap the cylinder and shake vigorously for 1 minute.

4) Observe color of solvent phase - if red, excess metals are present, and repeat test using a smaller volume of water.
The colors will range from green - blue-green - blue-grey - purple-red with increasing metal concentration.

5) If a green color was obtained, sensitivity can be increased by then adding 2M NH_4OH slowly until the thymol blue indicator incorporated in the buffer solution changes from yellow (pH 5.5 buffer) to blue (pH 8.5). Then add a few drops excess NH_4OH.
Shake again vigorously for 15 seconds - excess dithizone will dissolve in the now alkaline buffer, leaving metal dithizonates in the solvent forming a mono-color series from colorless to weak pink. (a yellow organic phase indicates that dithizone has oxidized).

6) Relative colors can be compared to laboratory standards of weak Zn solutions, or assigned some arbitary scale for field work.

Apparatus.

Eppendorf type dispensing pipettes, and containers as before.

Reagents.

1) dithizone solutions as before. If emulsification is a problem, carbon tetrachloride could be substituted for toluene.

2) 2M NH_4OH; metal free. Purify if necessary as for the alkaline buffer solution used in the previous test.

3) buffer solution: pH 5.5. (keeps indefinitely).
2M acetic acid. 114 ml glacial acetic acid to 1 liter of metal-free water.
2M sodium acetate solution: 164 g of anhydrous sodium acetate in 1 l. of metal-free water.
Mix 900 ml of 2M sodium acetate with 100 ml of 2M acetic acid. Add 2 g of sodium fluoride (to inhibit effect of Al ions at this pH), 2 g of ascorbic acid (to inhibit oxidation) and 10 ml of a saturated solution (or emulsion) of silicon antifoam in acetone (to inhibit emulsification and frothing from humic acids). Add a few ml of thymol blue indicator in alcohol.
Purify the buffer as described previously.

Note:

If frothing and emulsification from the humic rich waters persists, try adding a few drops of silicon antifoam dispersed in acetone directly to each sample prior to step 3).

APPENDIX B.

GRID POSITIONING TECHNIQUES

1. Terrain Difficulties

Because of the dense rain forest cover in much of the area, and lower ti-tree (leptospermum nitidans) scrub on more stony, higher altitude slopes, line cutting is mandatory for both access and pegging. These lines provide access for geophysical (mainly gradient array I P) and soil (auger) geochemical sampling at pegged stations. The flatter moraine covered areas typified by the Basin Lake grid pose less of an access and line pegging problem.

A major difficulty with this approach is that line-cutting and pegging costs $250 - 300 per line km with a typical productivity of ½ line km per crew-day.

Slope corrections are applied in the field, and pegs are flagged and labelled with aluminium tags.

Subsequently, the lines are surveyed and plotted onto enlarged topographic (contour) base maps.

Fill-in lines are cut where warranted by geophysical and/ or geochemical results.

The recent EZ line cutting appears to be geometrically accurate, resulting in parallel lines with stations referenced to the Australian Metric Grid, plotted on enlarged topographic sheets.

The earlier Mt Lyell lines,perhaps because of local terrain difficulties, are often diverging and contain local "dog-legs" - slope corrections in steep terrain cause a further problem.

Added to this is the extra cost of staff surveying all lines as a check on line cutting (usually done by contractors) by tape and compass.

2. Nominal vs. true grid coordinates

Mt. Lyell sometimes uses a local grid reference system for each grid, with each base line zero referenced to an intersection with an access track, which itself can be highly irregular due to topographic constraints. (eg White Spur Area, EL 9/66) .

This results in eastings and westings grid references, which can pose a problem if computer plotting of results is to be done.

Moreover, nominal grid locations would result in a computer plot of parallel lines which may bear no spatial relationship to the actual grid as plotted on the base maps.

Thus digitizing techniques would need to be used to convert all positions to their true, corrected grid references on the Australian Metric Grid, if computer plotting is undertaken.

3. <u>Location methods</u>

There are three potentially rapid methods of locating lines and access tracks, costeans etc to Australian Metric Grid coordinates.

1) orthophotography.

2) the Mini-Ranger electronic positioning system.

3) the Magnavox MX 1502 satellite surveyor.

4. <u>Orthophotography</u>

This relies on locating features on stereo air photographs, which are then optically modeled to produce a map base. The equipment used involves a stereoplotter with orthophoto attachment, and produces a rectified, "true to scale" photograph upon which the AMG grid (or any arbitrary grid) and contours may be superimposed, along with inked-in access tracks, bench marks, annotations of grid lines and numbers etc. This can be done at any convenient scale such as 1:10,000 or 1:5000, with the final orthophoto negative screened to produce a half-tone sepia on standard AO mylar sheet.

Thus dyeline copies of the photomap base, showing cultural features with superimposed contours and grid references can be produced at will and used for adding geological and geochemical information.

The number of stereo models and control points to be used increases with terrain complexity, but there should be ample H.E.C. benchmarks, trig. stations etc. in the area to provide good control from existing high-level photography without further surveying.

In practice the orthophoto device optically scans a narrow strip of terrain on the stereo-plotter, and electronically transposes the strip scene to rectified scale on a new negative. The complete image is built up of adjacent scan strips, the width of which (hence plotting speed and cost) is a function of terrain complexity and accuracy desired.

The accuracy obtained is more than adequate for exploration purposes.

A disadvantage of orthophotography in this terrain, is that in densely forested areas features such as cut lines and minor streams may not show up (if not seen on the normal air-photographs). Major features such as rivers, access roads and costeans would still be seen, however, and grid lines may be tied in to these.

Possibly the Hydro-electric Commission may already have orthophotomaps of some areas.

Orthophotomaps at regional scales (1:50,000) should provide a superior alternative to regional geologic compilations using mosaics.

Orthophotography services can be obtained from contractors such as Hunting Geology and Geophysics.

5. The Mini-Ranger System

This system, designed by Motorola (USA) is supplied through Marine and Aerospace Engineering Pty. Ltd., Suite 501A, 220 Pacific Highway, Crows Nest, N.S.W. 2065 (Mr. Ed. McCutchean, manager).

It works by triangulation of C band radar signals from a receiver/transmitter unit with built in antenna, referencing to two base stations which must all be in direct line of sight. The reference stations can be placed on hills (trig points), and the receiver/transmitter unit connected to its range console constitutes the mobile field station.

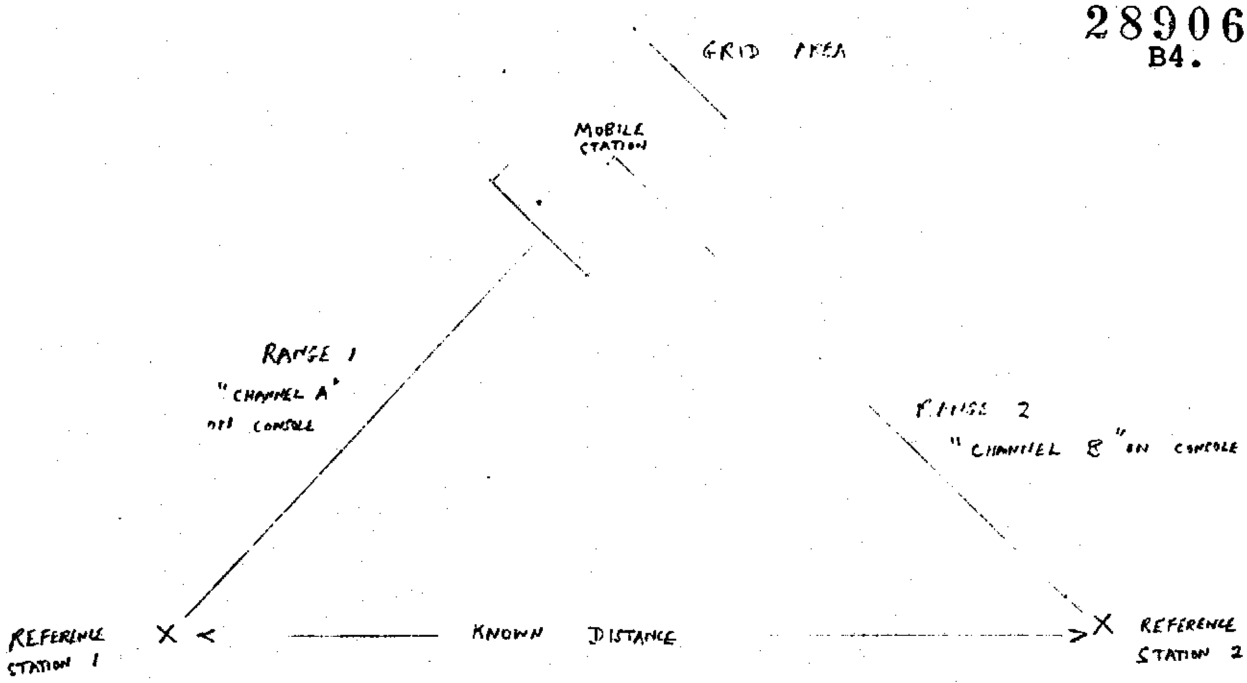
Maximum reliable range of the basic system is 37 km line of sight, where in free air conditions (no attenuation), range error is less than 3 meters.

The ranges to each base station appear as a digital readout in meters virtually instaneously on the range console (which, with the receive/transmit unit and connecting cable forms the mobile station).

If the grid area is comparatively small (say 2 km square) and triangulation is done to distant base (reference stations) of the order of say 20 km away, a single calculated slant range to the center of the area should be sufficiently accurate, irrespective of local topographic deviations within the grid.

Grid locations can then be obtained by calculation.

Alternatively, to go to nominated grid reference positions, the distant reference stations should be placed at right angles to the mobilo station, range settings can be pre-calculated,and the mobile station moved accordingly.



Extra reference stations are available with the basic unit so that any two of up to 4 stations can be interrogated - for example, where the first two stations are in a radar shadow due to topography.

Many sophisticated options, (described in the brochures) are available to expand this basic arrangement. eg) automatic plotting, up to 16 reference stations, extended range, airborne steering indicators for flying pre-set lines, data processors, printers and remote data links etc.

A major disadvantage is that the range console and its attendant receiver/transmitter unit, power supply and cables constitute the heavier and bulkier equipment relative to the lightweight reference stations.

1) Tracking mode.

An optional, but more expensive alternative, is to use the system in tracking mode. Here the 6 lb. reference station, with its attendant lightweight cable and mast, is operated with lightweight batteries (10 lb.) as the mobile station, and the heavier range console system with its heavier cable is located "permanently" as a base station. Range information is then produced at the distant site by an optional printer, or alternatively by remote data link back to the mobile (grid) site or office. Another means would be to have an assistant at the range console reference station in radio communication with the mobile crew, as a manual "data link".

2) Attenuation problems.

Rain forest canopy, particularly when wet, can cause severe attenuation of the radar signal, such that range error can be as great as 20-30 meters. If the attenuated signal is too weak for satisfactory operation, this will be displayed on the range console.

Attenuation can be handled as follows:

a) a hydraulic mast/tripod arrangement is available to hoist the 6 lb. receive/transmit unit with cable up to 30 ft above the ground. This should provide clear line of sight in many instances and overcome attenuation problems.

b) a signal strength meter can be supplied optionally and calibrated against signals supplied from a variable attenuator, to produce a nomogram of range corrections vs. signal strength. Then during routine operation, range results obtained are corrected for the signal strength measured at each site.

3) Equipment weight and configuration.

a) base stations - minimum of two required.

i) 6 lb. weight with built-in antenna, + 10 ft light-weight cable + tripod + power supply.

ii) Power supply: one pair 10 amp/hr. motor-cycle or aircraft type batteries on each station will operate for 1 day. These are connected in series for 24V operation.
A pair of 100 amp/hr. batteries (24V mode) will operate for 1 week, as the system switches to standby mode if readings are more than 30 min. apart.

b) mobile station (in normal use)

i) range console weighs 28 lb. and can be supplied in a heavy duty aluminium carrying case (22" x 22" x 11" dimensions) which also holds the transmitter/receiver cable for the R/T unit (mounted on mast). A light weight 50 ft cable is available. Total weight in case = 45 lbs.

ii) R/T unit with built-in antenna, in aluminium carrying case weighs 10 lb.

iii) telescopic (hydraulic) mast/tripod base with 30 ft extension (to mount R/T unit above tree canopy). This folds down to about 7 ft, and weighs 25 lb.

iv) power supply: two 24V aircraft batteries (approx 30 lb total weight) would supply one day's operation.

4) Prices.

a) basic system: 2 base stations and 1 mobile plus cables and mast = $31,000

b) spares: $ 5,000

c) extra base stations: $ 6,000 each

d) batteries - supplied by client.

e) tracking version (remote data link) available from overseas only (60 days delivery) for extra $15,000.

The basic unit is available ex stock, and can be leased or rented at 15% of equipment cost per month (90 days or greater) or 18% per month for less than 30 days.

The standard positioning system can be rented for demonstration purposes for as little as 1 week, at a cost of $225 per day. Training would be supplied in Sydney free of charge.

6. Recommendation

The equipment is expensive and may prove cumbersome if used in the normal mode in typical West Coast terrain.

However, when off-set against the cost of line cutting, it may prove more cost-effective in the long run if used in the tracking mode in conjunction with rapid reconnaissance geochemical surveys using A_0 or litter samples on uncut lines.

Such surface sampling can provide a rapid first pass coverage of new areas. Sample sites can be flagged, located by grid reference, and re-located with the positioning system where anomalous zones need to be followed up by detailed survey. Some less rigorous line cutting would still be required for access in many areas, but only those which prove anomalous need to be systematically line cut and pegged.

How well the system performs in actual field conditions remains to be seen. The basic system could be hired for 1-2 weeks with costs and performance trials shared by both joint-venture groups. This could be done in the tracking mode by having an operator relay the range information from the base station by radio to the mobile station. Only light equipment need then be carried.

Should it prove cost-effective, a longer term lease arrangement or purchase shared by both parties may be worth while.

7. <u>The Magnavox MX1502 Satellite Surveyor</u>. (see brochure sent with report)

This system requires an antenna-receiver assembly only, as it receives signals from any of 6 TRANSIT navigational satellites positioned by the U S Navy in 1964, and available to all users since 1967.

The satellites orbit the earth in fixed circular polar orbits at 1100 km altitude and 107 minutes duration, forming a "birdcage" enclosure around the rotating earth. Thus the observer passes under the orbit of each satellite, in sequence.

The satellites transmit signals at 150 and 400 MHz, the dual frequency allowing the removal of ionospheric refraction effects.

Each satellite pass is in view (horizon to horizon) for about 15 minutes, during which time it has moved approximately 7000 km.

The orbital pass is very accurately known and the ground receiver obtains the orbital parameters during each 2 minute interval (satellite navigation message). Estimated position is entered into the receiver via the keyboard (which incorporates a microprocessor). The receiver then computes the satellite position, calculates satellite-to-receiver ranges at the beginning and end of each Doppler frequency of the passing satellite until calculated and measured range differences agree.

The final output is that a digital readout of latitude and longitude is displayed on the first satellite pass to an accuracy of about 30 meters RMS.

Subsequent orbital passes will give a read-out of elevation as well as position, and the accuracy improves with each successive orbit to about 3-5 meters RMS error, after several passes.

At latitude 40^0 , normal time between successive satellite passes is about 75 minutes.

The microprocessor section of the receiver will convert positions to any datum (ie AMG, or local grids if desired).

The advantages of the system are its portability and ruggedness (receiver/processor = 19 kg, plus antenna unit 7.7 kg including tripod and case, plus a 12v car battery) - no reference stations are required.

Major disadvantages are high cost (US $48,500) and the waiting time between orbital passes. However, an extra series of NOVA satellites is due to be launched at the end of 1979, and this will reduce orbital intervals.

The system could probably be used best for locating key reference points or base lines, but would be too slow for positioning at each station.

The representatives in Australia are Hawker Pacific Pty. Ltd., P.O. Box 172 Yagoona, N.S.W. 2199 (Mr. David Cook).

APPENDIX C

Some notes on Magnetic Fractions of Heavy Mineral panned Concentrates, from discussion with Dr. W. C. Overstreet, U. S. G. S. Denver, April, 1971.

The theory of the method is that magnetics will, because of their crystal structure, contain substituted trace element impurities which reflect the geochemical background of the source rock. Unlike the normal stream sediments, the magnetite from weathered rocks ("saprolites") will not be as subject to loss by dilution as it is stable, forms long dispersion trains, and can be readily concentrated by panning and magnetic separation.

Drainage basins of the order of 10-30 sq. miles are selected on aerial photographs and the necks of these drainage areas selected as sample sites.

Locally, at the sample site, one usually selects alluvium in or adjacent to an active stream which is likely to have dropped its heavy mineral load due to sudden widening, presence of back-wash induced by rock bars or change of course. etc.

Thus one samples at a suitable site as one would for gold.

To maintain comparative results from stream to stream, portions of streams should be sampled such that hydraulic loads are always comparable; a good rule of thumb being to always select the portion where the largest 10% of cobbles is fist sized.

The alluvium is then sampled, discarding the pebbles. A large lipless pan is then 2/3 filled with about 25lb of alluvium which has been wet sieved in the stream to -10 mesh through a large steel punch plate. The clay is carefully dispersed by kneading and washed out until a gritty sand only remains. Panning must be done slowly and carefully, with little tilting and no jigging through screens, as some magnetite is very fine, and the aim is to retain all magnetite. Generally, the time taken is about four times greater than that for panning gold. It is possible to use a mechanical super-panner provided clays have been removed and

APPENDIX C (Cont'd.)

and the feed kept constant.

Panning is gradually reduced to a grey fraction where magnetites and spinels can no longer be readily retained. The concentrate is then cleaned out three times with a hand magnet, which will remove magnetite and highly magnetic ilmenite, gradually with a grain size of about 150 mesh.

The magnetic fraction ("magnetite") is then dried, finely ground if necessary, digested in hydrochloric acid and analysed in the geochemical laboratory.

A recommended USGS procedure for magnetite analysis has been given to me by Fred Ward of USGS Denver.

I would also suggest the further refinement of using a standard size container, such as a bucket, to consistently measure the same amount of -10 mesh sieved sample. Then, if the laboratory weighs the magnetite extracted, subsequent trace element contents can be normalised to take care of varying magnetite abundance. i.e.) 100 ppm in 1% magnetite is no more significant than 50 ppm in magnetitie comprising 2% as in both cases the partition of trace elements between silicate and oxide phase during igneous rock formation indicates the same original quantity of background trace element.

At the same time, the heavy mineral fraction, after magnetic separation should be stored in a container for future reference.

Binocular microscope examination for resistates such as andalusite, staurolite and garnet can give a clue to the presence of certain rock types and metamorphic aureoles up drainage, and in fact, Overstreet has developed techniques for rapid grain counting and mapping of metamorphic zones in highly weathered terrain using this approach. - Further details on this approach can be made available on request through N. J. Marshall.

345 samples of detrital magnetite from panned concentrates of alluvium from tens of thousands of square miles of Alaska were analysed for Cu, Ni, Pb, Zn, Ag, Bi, Co, Ni by the U.S.G.S.

APPENDIX C . (Cont'd.)

Many samples came from known mining camps, often 10 miles downstream from the mineralisation.

In the whole area, 24 known copper deposits occurred; and of the 24, 17 sample sites were anomalous in copper and the rest anomalous in either Pb, Zn, Ag, Bi, Co or Ni. Some difficulty was experienced with bismuth due to the very low backgrounds of 0.2 - 1 ppm and consequent difficulty in analysis.

The following table by Overstreet, (not yet published) shows the relationship between the known mineralisation and the anomalous element contents in the Alaskan magnetites.

074

Anomaly/ Known Mineral-isation	Cu	Pb	Zn	Ag	Bi	Co	Ni	Total deposits	No. of deposits showing only background (i.e. not anomalous)
Cu	17	9	16	9	1	6	5	24	7 N.B. all anomalies for other than Cu
Pb	9	7	7	7	1	2	2	11	4 all 4 anomalous for other than Pb
Zn	12	6	10	7	2	3	3	12	2
Ag	9	5	8	6	1	5	4	14	7
Bi	1		1		1			4	3
Co	1		1	1	1		1	1	1
Ni	1			1	1		1	1	0

The frequency relationship between known metal deposits (Classified as Cu-Pb-Ag etc. according to the prospectors estimate of the situation from old records) and anomalous element content in magnetites is shown below.

Anomaly/ Known Mnrlisation	Cu	Pb	Zn	Ag	Bi	Co	Ni	Total Deposits
Cu-Zn	2		2					2
Cu-Ag	2		1	1		2	2	4
Cu-Pb-Ag			1			1		1
Cu-Zn-Ag	1		1			1	1	1
Pb-Zn-Ag	1	1						1
Cu-Pb-Zn-Ag	6	4	5	5				6

289075

C4.

APPENDIX D.

RECOMMENDED LABORATORY PROCEDURES.

1. "Total heavy metals in rocks, soils (B and C horizon) and stream sediments.

Either aqua regia or perchloric/nitric digests can be used. If much perchloric/nitric work is undertaken (for organic materials), it may be preferable to standardize on this one procedure for all samples.

1) aqua regia digest.

To 0.200 g of fine (generally -80#) sample in 20x150 ml Corning 9820 culture tubes (rimless) graduated at 10 ml (these can be purchased ready graduated) add 3 ml of aqua regia. (Use an Oxford dispenser for the addition). Aqua regia = 3+1 conc. $HCl:HNO_3$. Heat on sand bath or aluminium heating block for several hours until only a bleached residue remains. Heat to near dryness. (say ½ ml remaining).
Add 10 ml of 1N (10%) HCl to the graduation mark and allow to warm gently to dissolve salts.
Mix contents by bubbling with a capillary stirrer connected to an aquarium pump.
Arsenic can also be determined on aliquots of the same solution. Compare on AAS with standards in 10% HCl.

2) perchloric/nitric digest."(wet ash)".

This is a suitable substitute for the aqua regia digest, and is necessary for treatment of organic rich A0 humus and litter samples.
To 0.200 g of sample in culture tubes as before, add 3 ml of 3+1 conc. $HClO_4$/conc.HNO_3 (previously mixed and added with Oxford dispenser). Place on cold (or lukewarm) heating block and allow temperature to rise gradually to 190° c. Brown NO_2 fumes will evolve first, thus pre-conditioning the sample with HNO_3 before the perchloric acid becomes hot and concentrated. Only hot conc. $HClO_4$ is dangerous with readily oxidizable matter - this procedure ensures that the reaction can proceed safely.
At 190°c, all HNO_3 has boiled off, and the perchloric acid will boil and reflux as dense white fumes to condense and run down the sides of the tube. Comparatively little $HClO_4$ enters the atmosphere.
After about 1 hour at this temperature, a clear solution will result, a white residue (silica and feldspar) will remain (all brown Fe oxide components leached out), and all organic matter will be oxidized.

Allow solutions to cool somewhat (but not to room temperature as salts will crystallize out). Add distilled water to the 10 ml graduation mark, allow solutions to warm again (to dissolve salts), then mix by bubbling air as before. Determine AAS elements by reference to standards in 20% $HClO_4$ (not HCl). Arsenic can be determined on aliquots of this solution.

Notes

1) always note color and relative abundance of any dark residues remaining. This can signify resistate minerals such as cassiterite or spinels.

2) always note occurrence and relative vigor of carbonate effervescence - this can be a valuable guide to wall-rock alteration.

3) always note any unusual flame colors seen for elements not normally analyzed for - eg) high Sr, Ca etc.

2. Total silicate attack.

The HF/$HClO_4$ attack commonly used requires expensive Teflon ware which precludes large batch operation. Moreover, potassium perchlorate is insoluble, so K cannot be determined unless evaporation to dryness with HCl is carried out.

The recommended procedure of an HF/aqua regia attack gives virtually equivalent results, and allows the use of inexpensive (20 cents each) polypropylene containers for large batch operation. This method has been used routinely by the author for 10 years on all classes of materials, except litter samples, and is thus a "near-universal" one substituting for aqua regia and perchloric/nitric acids.
Total base metals and silicate rock components (alteration elements) can all be determined in the one solution, along with arsenic on an aliquot of the same solution.

Samples of the apparatus used for digestion and handling the polypropylene vessels are being supplied with this report.

The use of HF/aqua regia maintains a low temperature oxidizing acid attack, and the inclusion of HF allows silicates to dissolve.

The digest is carried out at 120°-140° c, and there is no attack on the polypropylene.

Method.

0.200 g sample is placed in the polypropylene beaker, and 4 ml of a 2:1 HF/aqua regia mixture is added (aqua regia = 3:1 $HCl:HNO_3$).
The vessels are placed on an alumium heating black at 140° c, and the contents allowed to evaporate to dryness in an efficient fume cupboard,

With the aid of an Oxford dispenser, 10.3 ml of 10% HCl is added, the contents are warmed for 5 minutes to dissolve salts, then mixed by capillary tube air bubbler for about 1 second. The beakers are covered with "glad wrap" in their pre-numbered rack positions, ready for determination by AAS or colorimetry.

The digest is complete except for a few resistant spinels, cassiterite, graphite and resistate minerals such as garnet. Ca and Mg will cause precipitation of CaF_2 or MgF_2 and cannot be determined unless boric acid is added to complex excess fluoride ion.

The following elements can be determined routinely:-

Cu Pb Zn Co Mn Ni Fe As Cr (non spinel component)

K Na Rb Li Bi P Ti V Ca? Mo?
Any residues should be noted.

Safety considerations with HF demand efficient fume cupboards, protective goggles or eyeglasses, and plastic (not rubber) gloves.

3. 0.5N cold extractable metals. (for soils and stream sediments).

The sample is agitated periodically over a period of 3½ hours with 5% HCl at room temperature. The contents are allowed to settle and the supernatant solution read by AAS after 4 hours.

Care should be taken to maintain reasonably constant time and temperature conditions from batch to batch, and to avoid the formation of a concentration gradient between the sample/solution interface. The quickest and surest procedure would be to centrifuge the samples and decant the clear liquid into test-tubes for storage prior to determination.

4. Silver analyses.

With care, a detection limit of about 0.3 ppm in the sample can be achieved. This is more useful than the current 2 ppm detection limit.

1.00 g sample is digested to dryness, twice, with 4 ml of aqua regia (3 ml conc. HCl + 1 ml conc. HNO_3) in the small polypropylene beakers used for the HF procedure.
After the second evaporation to dryness, 10.3 ml of 50% HCl is added, the contents are warmed, mixed, then rewarmed and remixed again.
After settling, Ag is determined by AAS relative to standards in 50% HCl (use tantalum nebulizer), using simultaneous deuterium arc background correction.
If this is not available, sample absorbances are read for Ag and the absorbances of the batch re-read immediately after (ie. same flame conditions) using a hydrogen continuum lamp.

The background absorbance for each sample is subtracted from the nominal Ag absorbance prior to calculation of corrected Ag values.
At low silver concentrations near the detection limit, background effects, particularly from high Ca, can be severe and lead to misleading results if this procedure is not followed.

5. Lead analyses.

Normally this presents no problems, as Pb anomalies tend to give a high contrast.
However, in some of the West Coast stream sediments and glacial soils, Pb values of the order of 20 ppm or less can be noticeably enhanced by high background from elements such as calcium. The effect may be sufficient to report, say 8 ppm true Pb as "30-40 ppm" when uncorrected for background.
This might be a problem in some West Coast environments, and is worth monitoring on selected samples from time to time using background correction.
Higher Pb values, of the order of 1-2% or more in high sulfide samples may assay too low due to precipitation of $PbSO_4$ from an oxidizing acid attack, unless special precautions are taken.
As a precaution it is suggested that Pb in the Henty Fault Zone massive sulfide sample be analyzed by an independent laboratory, or by an independent technique such as gravimetric analysis, to check the routine AAS result.

6. Arsenic analyses.

The enclosed paper by the author details a suitable rapid colorimetric procedure. It is anticipated that there will be future demand for As analyses.
This procedure should be used initially. Ultimately, the author can provide a rapid (1 sample per minute) and interference free procedure and apparatus for arsenic which is more sensitive and convenient to use. It is based on hydride evolution and atomic absorption, but is superior to published methods in its sample throughput and tolerance to interferences.

7. Barium analyses.

Barite, ($BaSO_4$) can not be brought into solution with acids or complexing agents. Apart from determination in the solid sample (XRF or emission spectroscopy), its determination requires a fusion procedure which is time consuming. Hence XRF analysis is usually preferred.
However, barium occurring as carbonate or in silicates can be determined by acid solution, provided that sulfides are absent. Sulfides will convert to sulfates in an oxidizing acid attack, and form $BaSO_4$ precipitate - hence low AAS results in solution.

Barium occurs in the Rosebery footwall alteration series, not as barite, but as Ba substituting for K in the sericite crystal lattice.
Provided sulfides are absent, this Ba can be brought into solution by the HF based procedure detailed above, and determined by AAS (use salt ionization buffer and N_2O/acetylene flame).

Thus the Mt. Lyell laboratory could determine Ba by AAS in non-mineralized rocks for identifying wall-rock alteration haloes. Initially it is suggested that the rock samples collected from W. Hercules line 800 N, which have very high Ba values, be acquired and re-run for Ba by HF/aqua regia and AAS.

8. Cold extractable Mn selective leach.

Reactive manganese oxide coating stream pebbles is selectively dissolved (relative to Fe, which is dissolved to a minor extent) by reducing conditions at low pH. (ie. those that prevail in humic acid rich waters in the natural environment). Base metals coprecipitated with the MnO_2 (on aerial oxidation) are removed with the Mn in solution.

Place approximately 5 g of uncrushed, coated pebbles in beakers and add 20 ml of 0.1M hydroxylamine hydrochloride in 0.01M HNO_3. (6.95 hydroxylamine HCl in 1 liter of water containing 0.63 ml HNO_3. pH approx. 2).
Agitate intermittently at room temperature for 2 hours; then decant liquid into test tubes; so that the reaction is stopped at 2 hours.
Determine Cu Pb Zn Mn Co by AAS with results expressed as ppm in solution. Arsenic and extractable Ba can also be determined.

Notes.

1) Keep a portion of the original sample for any repeat determinations.

2) Run different batches at fairly constant temperature and time. Two different analytical runs on orientation samples 24207-9 produced results which were a factor of two different for Zn, but were relatively consistent in reflecting the same pattern. This indicates that extraction was not at equilibrium (literature reports claim Mn solution "in minutes"). Batches should be run according to drainage basin sampled.

3) Other methods such as ascorbic acid, hydrogen peroxide, warm hydrazine (Fe+Mn leach) or simply dilute HCl are worth experimenting with on orientation samples to check which gives the best response for contrast between anomaly and background.

A Modified Staining Technique for Carbonates in Thin Section

POTASSIUM ferricyanide and alizarin red *S* are frequently used as stains for distinguishing between carbonate minerals. Potassium ferricyanide in acid solution produces Turnbull's blue with ferrous iron and it used to be thought that dolomite could be distinguished from calcite on the basis that dolomite alone contained ferrous iron. Recently this has been shown to be incorrect[1], and it is now known that any carbonate mineral containing small quantities of ferrous iron will stain with potassium ferricyanide providing the carbonate can be made to react with an acid medium. Recent work[2,3] shows that alizarin red *S* in solution is probably the best method of distinguishing between the common carbonates.

Boiling, 30 per cent sodium hydroxide solution, as used by Freidman[2] for staining blocks and chips, has been found unsuitable for staining thin sections, as the mounting medium (Lakeside 70, Canada balsam) tends to dissolve. A weak hydrochloric acid solution does not attack the mounting medium. I have obtained satisfactory results with the procedure described here. A concentration of 3 per cent hydrochloric acid, or greater, at room temperature dissolves away the more soluble carbonates and hence is undesirable. At room temperature alizarin red *S* is most selective as a stain in a concentration of hydrochloric acid which falls between 1 per cent and 2 per cent. At the 1·5 per cent plus level the thickness of the thin section is greatly reduced and the staining becomes pale. At lower concentrations, the stain becomes so thick that it obscures the fine detail of the thin section. An important feature of the stain at the 1–2 per cent acid concentration is that with calcite a surface parallel to the *C*-axis is more deeply stained than one normal to that axis. This is important in fabric analysis where optic orientation patterns are required.

The potassium ferricyanide stain is successful over a range of acid concentrations, and as this solution is mixed with the alizarin red *S* solution the same acid concentration (1–2 per cent) is used. At room temperature, at these low concentrations, potassium ferricyanide does not react with siderite.

Distilled water must be used for making up all solutions and for washing off surplus stain from the thin sections after each stage of the procedure. Much more reliable results are obtained if the thin section to be stained is etched first (stage I of procedure). This pre-staining etch removes all grinding dust from the carbonate surface and is carried out for at least 10 and not more than 15 sec using 1·5 per cent hydrochloric acid. The etched section is then immersed in an acidified mixture of the two stains (stage II). Each stain works independently, and there is no mutual interference. If the now partially stained section is immersed in an acidified solution of alizarin red *S* for a few seconds the colour differentiation of the carbonates is increased further, but it is important not to leave the section longer than 15 sec in the solution (stage III). After rapid but careful washing of the section in distilled water it is important to dry the stained surface as quickly as possible because the stain is relatively soluble in water. It is important not to touch the stained surface when drying as it is purely a surface precipitate and is easily rubbed off. To preserve and protect the now dried stain, during mounting or remounting, a layer of 'Durofix' is painted on to the surface with a soft camel-hair brush. The 'Durofix' is diluted with amyl acetate, in the ratio 'Durofix' : amyl acetate = 1 : 3, which readily evaporates, and when this layer is completely dry it has a refractive index very close to 1·54.

The details and consecutive stages of the procedure are shown in Table 1.

The distinction between dolomite and calcite, of which most ancient limestones are composed, is of considerable importance in limestone petrology. The modified staining technique described not only gives positive colour differentiation of these two important carbonate minerals but also, because of their different solubility in hydrochloric acid, gives a difference of thickness in thin section. Calcite is etched to approximately 15μ thickness while dolomite remains at 30μ thickness; this difference is readily observable with polarized light.

J. A. D. DICKSON

Department of Geology,
Queen Mary College, London, E.1.

[1] Evamy, B. D., *Sedimentol.*, 2, 164 (1963).
[2] Freidman, G. M., *J. Sediment. Petrol.*, 29, 87 (1959).
[3] Warne, S. S. J., *J. Sediment. Petrol.*, 32, 29 (1962).

Table 1

Procedure		Time	Carbonate	Result
Stage I	Etching 1·5% HCl	10–15 sec	Calcite Ferroan calcite	Considerable etch
			Dolomite Ferroan dolomite	Negligible etch
Stage II	Staining* 0·2 g A.R.S. per 100 c.c. 1·5% HCl 2·0 g P.F. per 100 c.c. 1·5% HCl Mixed in ratio A.R.S. : P.F. = 3 : 2	30–45 sec	Calcite	Very pale pink—red depending on optical orientation
			Ferroan calcite	Very pale pink—red Pale blue—dark blue Two superimposed give Mauve—purple—royal blue
			Dolomite	No colour
			Ferroan dolomite	Pale—deep turquoise depending on ferrous content
Stage III	Staining 0·2 g A.R.S. per 100 c.c. 1·5% HCl	10–15 sec	Calcite Ferroan calcite	Very pale pink—red
			Dolomite Ferroan dolomite	No colour

* A.R.S. = Alizarin red *S*. P.F. = Potassium ferricyanide

METALLURGY

Identification of a Beta-Tungsten Phase in Tungsten–Rhenium Alloys

PHASE diagram equilibrium studies in the binary tungsten–rhenium system show the presence of two phases over the range 0–65 wt. per cent rhenium at 1,500° C (ref. 1). A terminal solid solution having a body-centred cubic structure exists from 0 to about 27 wt. per cent rhenium, and a phase having a tetragonal sigma-type structure is found in the composition range 43–65 wt. per cent rhenium. In this investigation, alloys containing 13–45 wt. per cent rhenium prepared by vapour deposition

CKNOWLEDGEMENTS

The author thanks the Directors of Anglo American Prospecting Services Pty.) Ltd. for permission to publish this paper, A.A. Levinson, A.W. Rose, nd his colleagues for critically reading the manuscript, Anne Westoby for raughting the figures, Minex Laboratories for performing the analysis and the)'Okiep Copper Company for permission to publish the photograph of Gams-erg.

REFERENCES

Beeson R., Herzberg W. and Frick A., 1975. Geochemical orientation studies of base metal occurrences in the North-western Cape Province. Ann. Geol. Surv., Dep. Mines, S. Afr., 10, 1973–74.

taff O'Okiep Copper Company Ltd./Newmont South Africa Ltd., 1975. The Gamsberg zinc deposit. In: Pre-Congress Excursion Guide Book No. 2. Geol. Soc. S. Afr., 16th Congr., Stellenbosch, June-July 1975.

COLORIMETRIC DETERMINATION OF ARSENIC IN GEOCHEMICAL SAMPLES

N.J. MARSHALL

Australian Selection (Pty.) Ltd., Sydney, N.S.W. (Australia)

(Received March 2, 1978; revised and accepted September 11, 1978)

ABSTRACT

Marshall, N.J., 1978. Colorimetric determination of arsenic in geochemical samples. J. Geochem. Explor., 10: 307–313.

A colorimetric method and apparatus for the determination of arsenic in batches of geochemical survey samples is described. The powdered material can be digested with a perchloric/nitric acid mixture, or most conveniently by an HF/aqua regia attack utilizing aliquots from the same acid solution as used for routine multi-element atomic absorption analyses. Aliquots are treated with potassium iodide and stannous chloride to reduce arsenic to the trivalent state, and arsine is liberated by the action of zinc pellets. The arsine is absorbed in a solution of silver diethyldithiocarbamate in chloroform-quinoline, the reaction being carried out in batches using very simple, inexpensive apparatus which is easily constructed. Detection limits are variable according to aliquot quantities taken, but in routine use working ranges of 1–800 ppm As are readily achieved. Coefficient of variation is 6.6% at the 5 μg As level. The method is shown to be virtually free from matrix interferences commonly encountered in gossans, soils, rocks and many ores. At least 100 powdered samples can be analyzed per man-day.

INTRODUCTION

Arsenic is a widespread constituent of many types of mineral deposits and under many conditions is a suitable indicator for over twenty elements with which it may be associated (Boyle and Jonasson, 1973). Arsenic geochemistry thus has widespread application in investigation of primary dispersion, as well as in secondary dispersions where it is usally fixed in gossans, soils and stream sediments as ferric arsenate. In this form it is fairly resistant to leaching and is therefore capable of giving excellent high contrast anomalies in highly weathered terrain such as the Western Australian Shield. It is an almost ubiquitous associate, often with tin and barium, of volcanogenic massive sulfide deposits whose geochemical signatures can be recognized by studies of gossan geochemistry.

An excellent review of arsenic geochemistry has been given by Boyle and Jonasson (1973).

Although atomic-absorption-based procedures via hydride evolution through the use of sodium borohydride reductant have become popular in recent years (Thomson and Thomerson, 1974; Aslin, 1976), colorimetric methods offer certain advantages in batch productivity and simple instrumentation.

However, little has been published on geochemical applications and the effect of potential interelement interferences at the levels likely to be encountered in real geochemical samples, apart from the work of Gastinger (1972) who established concentration limits for Fe, W, V, Hg, Co, Ni and Cu in solution, and noted serious interferences from Hg, Co and Ni.

Colorimetric methods necessitate a prior separation/concentration step; and of the available approaches such as solvent extraction, halide distillation, coprecipitation or hydride evolution, the latter seems most convenient where it can be reacted directly with a colorimetric reagent to form a strongly colored complex.

Of the several colorimetric methods proposed, the old Gutzeit and Marsh tests are only semiquantitative, the modified molybdenum blue method (Portmann and Riley, 1964) is complex and subject to serious interferences from traces of phosphate and silicate, and the silver diethyldithiocarbamate in pyridine method (Vasak and Sedivec, 1952; Liederman et al., 1959) is the most convenient and popular.

In the latter method, the carrier solvent, pyridine, plays an essential role in acting as a nitrogen lone pair donor in the reaction between silver diethyldithiocarbamate (AgDDC) and arsine.

More recent variants of this reaction avoid the use of pyridine, with its unpleasant, pungent vapor by substituting other donor group compounds such as brucine (Geological Survey of Canada — in Aslin, 1976), *l*-ephedrine (Kopp, 1973) or quinoline (this paper) in chloroform as solvent.

EXPERIMENTAL

Quinoline (C_9H_7N) (with an extra benzene ring) is the next cyclic amine after pyridine in the series, and because of its higher molecular weight it is an oily viscous liquid with a rubber-like odour. In use it is diluted with chloroform, and gives identical sensitivity and behaviour to AgDDC in pyridine with none of the inconvenience of that reagent. The pale yellow reagent solution absorbs strongly at wavelengths below 430 nm but is virtually optically transparent at 545 nm, the wavelength at which the red-brown arsenic complex is determined.

Arsenic in the sample solution is brought into solution with an oxidizing acid attack, under which conditions potential losses by volatilization of the trichloride are prevented. Either aqua regia or perchloric/nitric acids can be used, but it has been found most convenient to take aliquots of a 10% HCl leach following total solution and subsequent evaporation to dryness at 110° C by an HF/aqua regia digest.

In the presence of matrix elements, recoveries are identical with this procedure, which has the advantage that it is amenable to large batch processing using inexpensive polypropylene vessels. Since total solution of the sample takes place (except for traces of resistant minerals such as graphite, cassiterite and spinels), the resultant solution is suitable for determination of a wide spectrum of major, minor and trace elements in addition to arsenic.

Certain types of silicified gossans sometimes leave a brown, iron-rich residue after perchloric/nitric digest, and since arsenic and other trace elements in gossans are usually coprecipitated with iron, the presence of an iron rich residue introduces a degree of uncertainty. For such situations, the HF/aqua regia attack is preferred.

In routine practice, 0.200 g of finely pulverized sample is heated with 4ml of a mixture of 2 parts HF (40%) and 1 part aqua regia (3 + 1 conc. HCl/HNO_3). Solution generally takes place within 30 minutes, this is then allowed to evaporate slowly (110° C hot-plate temperature) to dryness over a period of about 2 hours, with volatilization of SiF_4 and excess acid. The residue is then taken into solution by adding 10 ml of 10% HCl and warming. This operation is conveniently handled in large batches using custom made polypropylene vessels of 15 ml capacity with appropriately designed racks and heating blocks.

A 5 ml aliquot of this solution is placed in the arsine generator test tube, and 2 ml of Fe/KI solution followed by 2 ml of $SnCl_2$ solution added to reduce As^{5+} to As^{3+}. In the presence of high ferric iron matrix, we have found erratic recoveries of arsenic which were traced to incomplete reduction to trivalent arsenic at this step.

Siemer et al. (1976) studied the reduction of As^{5+} to As^{3+} by KI and found it to be time dependent with the concentration of HCl present. For example, a 1.3 M HCl solution took 11.3 minutes to reduce 10^{-7} M As^{5+} to As^{3+} using 0.14 M KI.

Gastinger (1972) found that Fe concentrations as low as 0.19 mg/ml interfered unless $SnCl_2$ exceeded 7.27 mg/ml in the final solution.

By warming the solution during the addition of Fe/KI and $SnCl_2$ reagent solutions, complete reduction is assured and consistent recoveries were obtained.

After cooling, 5 ml of 10% HCl/1.5% EDTA solution is added, followed by four Zn pellets (arsenic free, Merck).

Arsine (AsH_3) and hydrogen are then evolved by the action of zinc on the acid solution.

Excess ferrous ion is incorporated with the potassium iodide as this acts as an antipolarizing agent and promotes continued formation of nascent hydrogen in the presence of matrix heavy metals.

The use of glass wool impregnated with lead acetate to scrub the gas stream of H_2S is not necessary as any sulfides present will be oxidized to sulfate in the acid attack.

The generated arsine is bubbled through an 8-mm thick-walled capillary glass tube of 1—2 mm bore which is almost closed off at the end to form a pin-hole aperture. This tube fits inside a 12 (O.D.) × 150 mm test tube containing 3 ml of the AgDDC solution which it displaces well up the tube to provide a long, efficient absorbent column (see Fig.1). The same absorbent tube can be used, with a ½" adaptor, as an absorption cell for optical density readings in a Bausch and Lomb "Spectronic 20" spectrophotometer, thus providing a convenient system for rapid geochemical survey analysis.

Comparative tests with more eleborate gas absorption apparatus confirmed that absorption is virtually complete using this simple and convenient apparatus.

A routine batch of 50 standards showed that the coefficient of variation was 6.6% at the 5 μg As level.

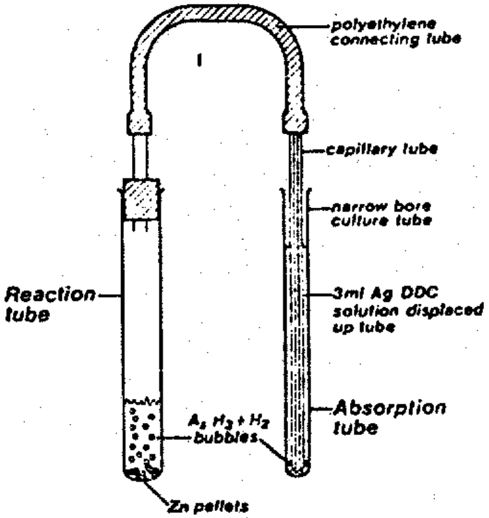


Fig.1. Arsine generator/absorber apparatus.

INTERFERENCE STUDIES

An amount of 2 μg As (as 1 ml of 2 ppm standard As^{5+} solution in 10% HCl) was added to a series of test tubes to which 2000 μg (as 2 ml of 1000 ppm solution) of each of Cu, Co, Ni, Pb, Mn were separately added, followed by 2 ml of the Fe/KI solution, 2 ml of $SnCl_2$ solution and 5 ml of 10% HCl.

The solutions were treated by the procedure described above, and optical densities of AgDDC solutions in chloroform/quinoline measured relative to that obtained by evolution from a pure 2 μg As standard in the absence of matrix addition.

Only 80% recovery was obtained for the Ni matrix solution and 75% for the Pb matrix solution under these conditions — other recoveries were within the experimental error of the technique. Gastinger (1972) reported severe interferences, however, for Ni and Co in his procedure.

To extend the capability of the technique to ores and high base-metal gossans without the need for preliminary separations, EDTA (1.5%) was then incorporated in the 10% HCl addition to act as a complexing agent for matrix cations.

As this does not involve any extra manipulative steps the use of EDTA was proposed in the routine procedure and interference tolerances were then tested for a wider range of elements.

METHOD

Add 2 ml of matrix interferent solution + 1 ml of 2 ppm As^{5+} standard in 10% HCl to test tubes. Add 2 ml of Fe/KI solution and warm, followed by 2 ml of $SnCl_2$ solution whilst hot. Allow to cool, add 5 ml of 1.5% EDTA in 10% HCl. Add four Zn pellets and absorb arsine generated in 3 ml of AgDDC solution (see Fig. 1). Determine absorbance of solution in reagent tube at 545 nm after 45 minutes gas evolution. Calibrate by evolving arsine from standard As^{5+} solutions containing 0—15 μg As and plotting a straight-line Beer's Law graph of absorbance vs. concentration.

For routine determinations on geochemical samples, take 1—5 ml aliquots of the sample digest (X 50 dilution factor) previously described and follow with additions of Fe/KI, $SnCl_2$, and EDTA solutions.

Optimum working ranges are 1—160 ppm As in the sample for a 5 ml aliquot, and 5—800 ppm for a 1 ml aliquot.

RESULTS

Table I lists the percentage recoveries for 2 μg As with various levels of potential interferents using the above method.

TABLE I

Interferent	Level (μg)	% As recovery
Na, K, Mg, Ca, Al, Fe^{3+}	20,000	95—100
Ti, V, Cr, Mn, Co, Ni, Cu, Pb, Ba, Sr, P, Mo, Bi, U	2000	90—100
Ag, Au	200	95—100
Ni + Cu + Zn + Mn + Pb	200 of each	90—100
Hg	200	120
Sb	200	120
Sb	100	95—100
Se	200	20— 50
	100	50
	50	70— 90
	10	95—100
Te	200	55
	10	80
	5	100
W	2000	45— 65
	1000	70
	500	80

Excess Cl^-, I^-, SO_4^{2-}, NH_4^+, Sn^{2+}, Fe^{3+} and Zn^{2+} are already present in the analyte solution and do not interfere

Some significant interferences gave erratic recoveries on repeated tests, and hence ranges are indicated.

Under the recommended operating conditions, and in the presence of EDTA, only Se, Te and W caused severe suppression at the levels tested above, whereas a slight enhancement was noted for Sb and Hg.

1000 μg Sb gave a reading equivalent to 0.8 μg As; however, after allowing for this impurity an enhancement of 120% was obtained.

Similarly, an enhancement was noted for Hg which on blank testing proved to be arsenic free. The reason for these enhancements which were consistently reproduced is not known, but in practice such As/Sb and As/Hg levels would not be a problem in normal geochemical samples.

DISCUSSION

If a 5 ml aliquot of sample solution is taken from the recommended digest (0.200 g in 10 ml) a dilution factor of 10X applies.

Thus the interference studies demonstrate that 20 ppm As in the sample can be determined in a sample matrix containing at least 20% of Na, K, Mg, Ca, Al of Fe^{3+} or 2% Ti, V, Cr, Mn, Co, Ni, Cu, Pb, Ba, Sr, P, Mo, Bi, U or 0.2% Ag or Au.

A gossan or low-grade ore containing 20 ppm As and 2000 ppm each of Ni, Cu, Zn, Pb, Mn would present no problem for trace arsenic determination.

In practice, it would be most unusual for samples to contain more than 5 times more selenium than arsenic, or 2½ times more tellurium, and analysis can be undertaken provided these interferent/arsenic ratios are maintained. High amounts of tungsten as in tungsten ores could present a problem, however.

Productivity is of the order of 200—300 samples per day if operators work in pairs and use rapid reagent dispensing equipment.

REAGENTS

(1) *$HClO_4/HNO_3$.* Three parts 72% perchloric acid plus 1 part concentrated nitric acid AR grade.

(2) *Fe/KI solution.* 14 g ferrous ammonium sulfate hexahydrate plus 20 g potassium iodide dissolved in 400 ml of approximately 3% H_2SO_4. Add trace of ascorbic acid to prevent oxidation.

(3) *$SnCl_2$ solution.* Prepare a 5% solution of $SnCl_2 \cdot 2H_2O$ in 50% HCl by dissolving in hot concentrated HCl first and then adding equal volume of water. Store in presence of tin metal.

(4) *Zinc.* Arsenic-free grade pellets, Merck.

(5) *HCl/EDTA solution.* Dissolve 1.5% EDTA, disodium salt in hot distilled water and then add hydrochloric acid to bring acidity to 10%. Prepare fresh daily as EDTA crystallizes out on standing.

(6) *Arsine reagent solution.* Dissolve, with warming, 1.000 g of silver diethyldithiocarbamate (Merck) in 300 ml chloroform + 100 ml quinoline. Store under refrigeration and keep away from light.

N.B. The reagent solution should be pale yellow in color; avoid the use of old stocks of quinoline (brown), or silver diethyldithiocarbamate (dark yellow powder).

Silver diethyldithiocarbamate can be readily prepared in pure form as follows: Dissolve silver nitrate and sodium diethyldithiocarbamate in water in separate beakers. Add an excess of sodium diethyldithiocarbamate to the silver nitrate solution and filter off the creamy yellow precipitate using Buchner funnel. Wash with distilled water and dry in desiccator — keep away from strong light.

Purify as follows: Dissolve to make saturated solution in hot chloroform, then filter through siliconised (phase separating) filter paper to remove solids and water. Add excess ethyl alcohol to cold filtrate, allow compound to crystallize out, filter through Buchner funnel and suck dry. The product is a pale yellow crystalline solid with a soapy feel, and is similar in appearance to the sodium salt. It should be stored in the dark.

ACKNOWLEDGEMENTS

The permission of the directors of Australian Selection (Pty.) Ltd. to publish this paper is gratefully acknowledged.

REFERENCES

Aslin, G.E.M., 1976. The determination of arsenic and antimony in geological materials by flameless atomic absorption spectrometry. J. Geochem. Explor., 6: 321—330.

Boyle, R.W. and Jonasson, I.R., 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. Geochem. Explor., 2: 251—296.

Gastinger, E., 1972. The spectrophotometric determination of arsenic with silver diethyldithiocarbamate. Mikrochim. Acta, 4: 526—543.

Kopp, J.F., 1973. *l*-ephedrine in chloroform as a solvent for silver diethyldithiocarbamate in the determination of arsenic. Anal. Chem., 45: 1786—1787.

Liederman, D., Bower, J.E. and Milner, O.I., 1959. Determination of arsenic in petroleum stocks and catalysts by evolution as arsine. Anal. Chem., 31: 2052—2055.

Portmann, J.E. and Riley, J.P., 1964. Determination of arsenic in seawater, marine plants and silicate and carbonate sediments. Anal. Chim. Acta, 31: 509—519.

Siemer, D.D., Prabhakaran, K. and Vibhakar, J., 1976. Optimization of arsine generation in atomic absorption arsenic determinations. Anal. Chem., 48: 836—840.

Thomson, K.C. and Thomerson, D.R., 1974. Atomic-absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by utilizing the generation of covalent hydrides. Analyst, 99: 595—601.

Vasak, V. and Sedivec, V., 1952. Colorimetric determination of arsenic. Chem. Listy, 46: 341—344.

08

083

289086

Journal of Geochemical Exploration, 10 (1978) 193—194 193

hem. Explor.,

Texas and
:. Pet. Geol.,

ranslation from

orado. Am. J.

Publishing,

r hydrogeo-
chem. Explor.

Short Note

A TUBULAR-SCOOP SAMPLER FOR STREAM SEDIMENTS

GARY C. CURTIN

U.S. Geological Survey, Denver, Colo. 80225 (U.S.A.)

(Received May 16, 1978; accepted June 21, 1978)

ABSTRACT

Curtin, G.C., 1978. A tubular-scoop sampler for stream sediments. J. Geochem. Explor., 10: 193—194.

A stream-sediment sampling tool is described.

INTRODUCTION

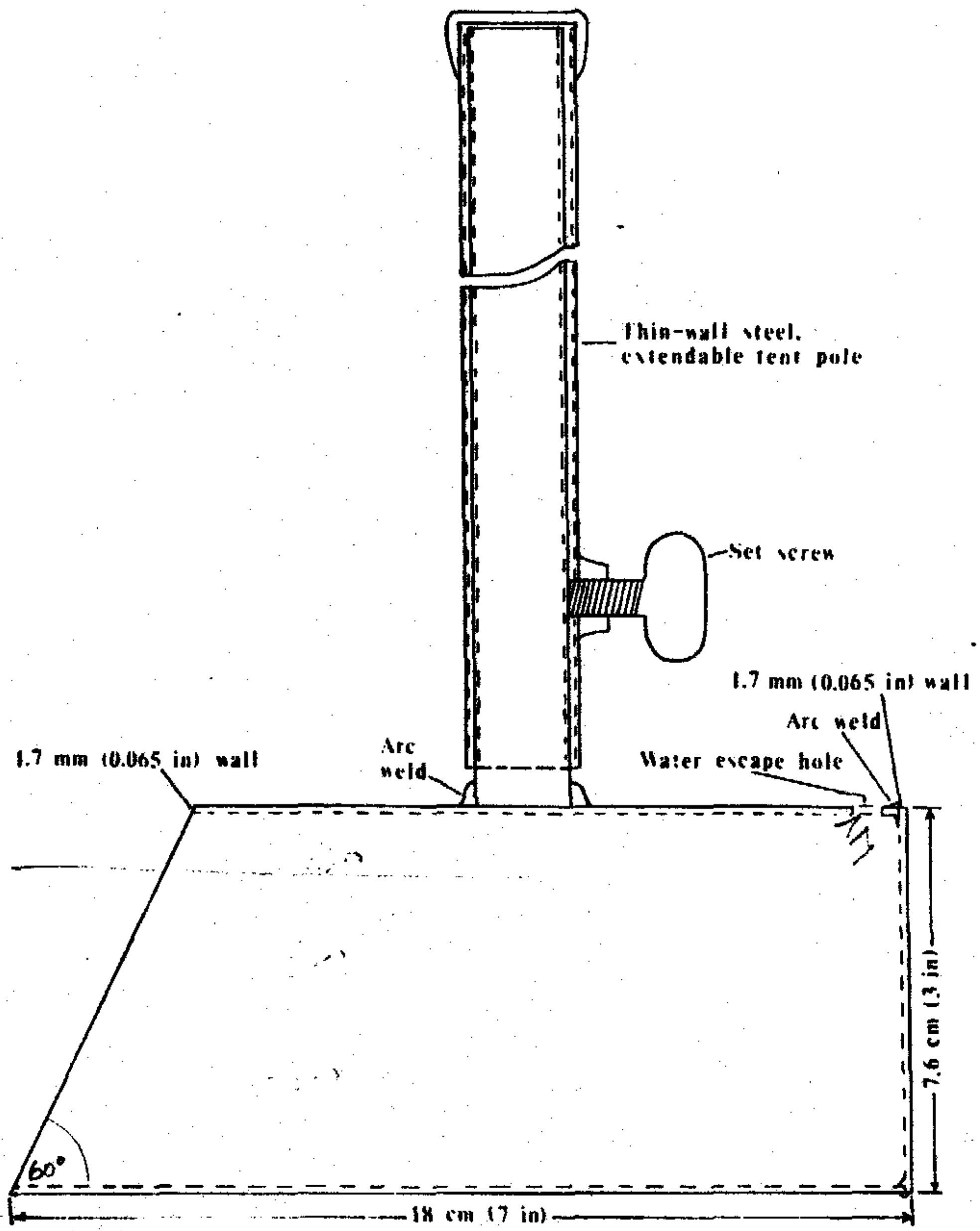
The sampler described here was developed for use in deep-channeled streams draining permafrost areas in Alaska. It has, however, also proven useful for stream-sediment sampling in swiftly flowing streams draining rugged, mountainous areas. The sampler has an extendable handle that allows samples to be collected from depths of more than 2 m (6 ft). It is also sturdy enough to be used to pry cobbles from "armored" stream beds, so that the fine sediment trapped between the cobbles can be collected. The sampler allows the collection of stream sediment with a minimum loss of sample — especially in deep, swiftly flowing streams.

DESCRIPTION

The sampler, shown in Fig. 1, consists of: (1) an 18-cm (7-in.) length of seamless steel tubing that has an outside diameter of 7.6 cm (3 in.) and a 1.7-mm (0.065-in.)-thick wall; (2) a 1.7-mm (0.065-in.)-thick steel plate to close one end of the tubing; and (3) an extendable tubular-steel tent pole with set screw. The sampler scoop is constructed by cutting one end of the 18-cm piece of tubing at an angle of approximately 60° (Fig.1), and then welding a circular piece of 1.7-mm-thick steel plate to the other end of the tubing. The collapsible tent pole is welded to the scoop as shown in Fig.1. A small hole is

08

289087



SECTION
Fig. 1. ~~Plan~~ view showing dimensions of sampler.

drilled through the top of the scoop near the rear plate to allow the escape of water as the sediment sample is being collected. Before the sampler is used, the welds are smoothed to remove any small pieces that could break off and contaminate the samples.

Journal of Geochemical Exploration
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

AN AUGER-SLEEVE SAMPLER FOR STONY SOILS*

G.C. CURTIN and H.D. KING
U.S. Geological Survey, Denver, Colo. (U.S.A.)
(Accepted for publication September 1, 1972)

ABSTRACT

Curtin, G.C. and King, H.D., 1972. An auger-sleeve sampler for stony soils. *J. Geochem. Explor.*, 1: 203–206.

A sleeve-type auger for sampling in stony soils is described.

INTRODUCTION

An auger-sleeve soil sampler was developed by us as an improvement over existing barrel-type samplers to facilitate the collection of alpine and subalpine soils during geochemical exploration. These soils characteristically are poorly consolidated, have weakly developed profiles, and contain a high percentage of pebbles and cobbles – as much as 60% in places (Retzer, 1962, p.34). In such soils, we have found it difficult to use ordinary soil augers to collect soil samples from known depths that are free from contamination by material from above. The auger-sleeve soil sampler described here solves this problem in geochemical sampling.

DESCRIPTION

This sampler consists of: (1) a probe (Fig.1A, 2A) made from ½-inch-diameter aluminum rod; (2) a sleeve (Fig.1B, 2C and D) of welded steel tubing, 2³/₈ inches in outside diameter with walls ¹/₁₆ inch thick, and a removable collar for the sleeve; and (3) a 2-inch-diameter barrel auger with a removable handle (Fig.1C, 2B) which was obtained from Soiltest, Inc., Evanston, Ill., U.S.A. To reduce weight the auger was altered by substituting an aluminum shaft, 27 inches in length, for the steel shaft. The collar (Fig.2D) was made by cutting a 4-inch section of the welded steel tubing along its length, then inserting a 1¾-inch section of the tubing inside the split section as a flange to fit the top of the sleeve, and finally welding the two sections together and welding a plate (¹/₈ inch thick and ¾ inch wide) over the split. Two 5½-inch sections of ¾-inch-diameter steel pipe were welded to the collar as handles. The removable collar makes it easier to pack and carry the sampler. If compactness

*Publication authorized by the Director, U.S. Geological Survey.

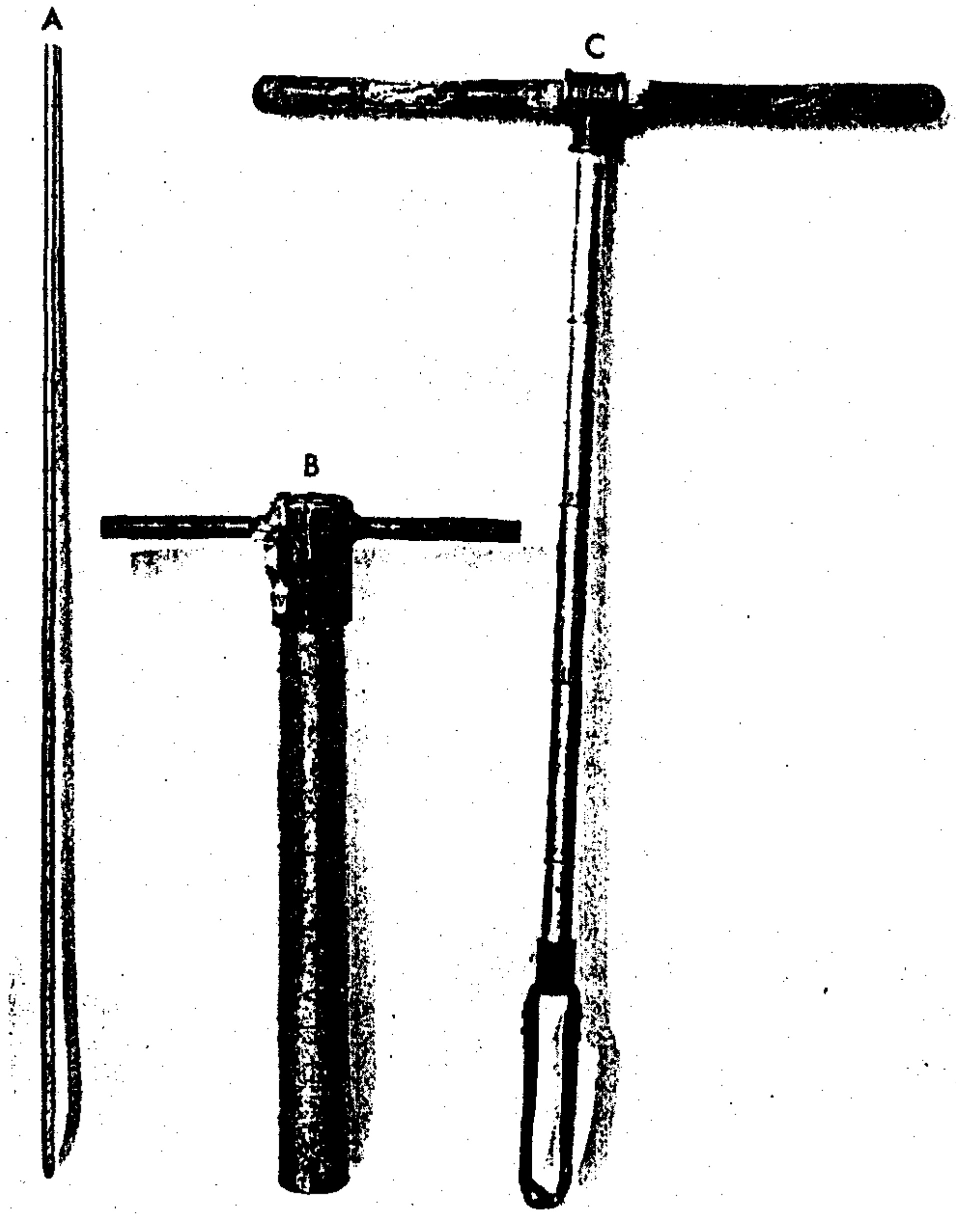


Fig. 1. Parts of the sampler: A, aluminum probe; B, sleeve with removable collar; C, auger.

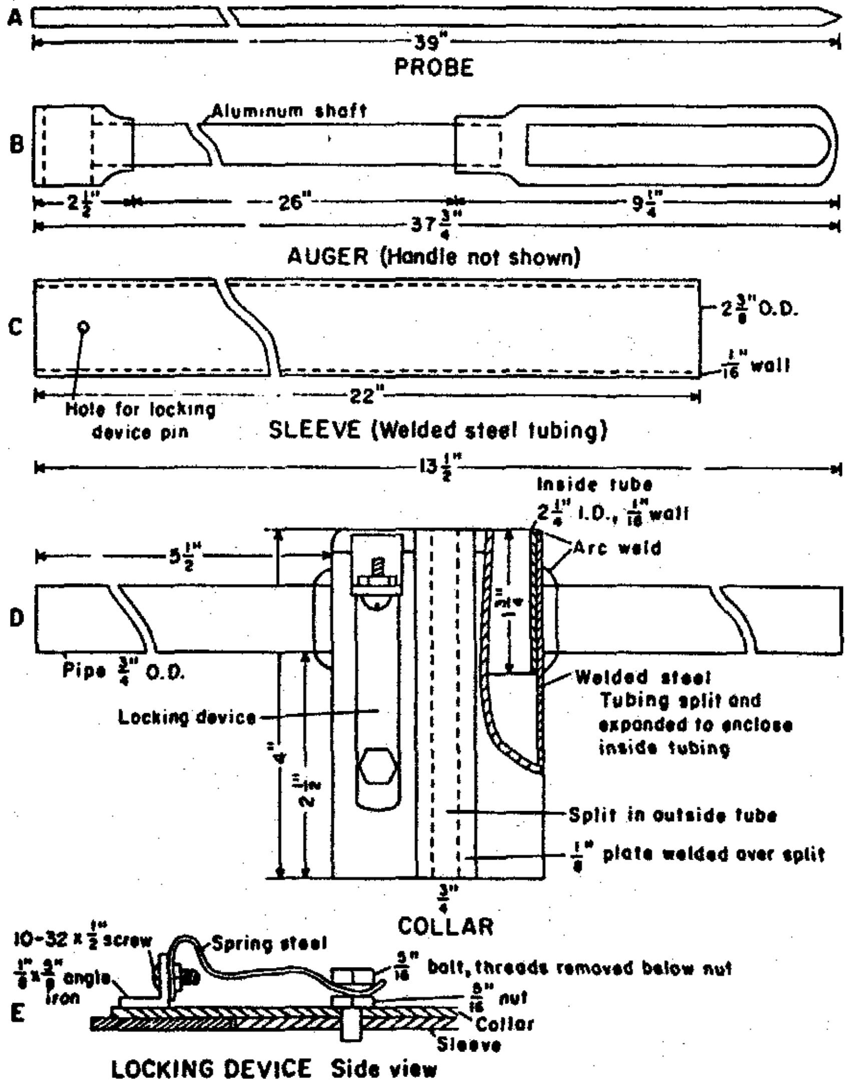


Fig.2. Plan view showing dimensions of the sampler assembly.

is not a consideration, however, a simplified collar and handles can be welded directly to the sleeve.

A locking device (Fig.2E) is used to lock the collar to the sleeve. It consists of a pin which penetrates matching holes in the collar and the sleeve. The pin is mounted on a piece of spring steel and the unit is attached to an angle bracket which is welded to the collar. When the collar and sleeve are locked together, the sleeve can be easily removed from the hole or rotated during insertion into the hole. An inch–foot scale was scribed on the probe, the sleeve, and the shaft of the auger.

289091

The use of this sampler expedites collection of uncontaminated soil samples because the relatively small diameter of the auger allows it to be driven easily between cobbles and to push them out of its path so that the sleeve can be inserted to the bottom of the hole.

Samples of soil are collected by first probing the soil with the aluminum rod to find a spot which is free of large cobbles or boulders within the depth range to be sampled. The auger is then inserted into the sleeve and turned until it has penetrated the soil the length of the auger barrel. The sleeve is then forced to the bottom of the hole by pushing on the collar handles, the auger is removed, and the sample is collected. The auger is re-inserted in the sleeve and the process is repeated.

REFERENCE

Retzer, J.L., 1962. Soil survey of Fraser alpine area, Colorado. *U.S. Dept. Agric., Forest Serv. and Soil Conserv. Serv., Soil Surv. Ser.* 1956 (20), 47 pp.