KIDD CREEK MINES LIMITED

GEOCHEMISTRY WORKSHOP MANUAL

APRIL 1983

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KIDD CREEK MINES LIMITED
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(APRIL 1983)

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INTRODUCTION

The purpose of this manual is to initiate an open discussion of the use of geochemistry on Kidd's mineral exploration programs throughout Canada. Since joining Kidd, I have had a chance to discuss with a number but not all of you the use of geochemistry specific to your projects, visit some of you in the field and hear a few of the projects reviewed at the managers meeting. I have found that while geochemistry is, for the most part, being appropriately utilized there is a need for refinement and updating to optimize the effectiveness of geochemistry within our exploration programs. Therefore, I would like to approach geochemical workshops as forums: to put forward comments on the status of geochemistry within Kidd and to present recommendations to upgrade the effectiveness and hopefully success of geochemistry in locating mineral deposits.

It is certainly not possible to cover the entire scope of exploration geochemistry in the context of a workshop. Rather, the plan is to review some of the basic principles of geochemistry which need re-emphasis and to go into more detail in specific problem areas such as:

1. Sample collection methodologies,
2. Field data acquisition,
3. Quality control of analytical data,
4. Data interpretation and
5. Data management, documentation and archiving.

These facets of geochemistry are clearly all interrelated, but to successfully achieve the last two we must improve our performance in the first three. In other words, meaningful interpretations require good data.

Remember, I am always available for you to consult regarding the use of geochemistry on your projects. If you have a question or problem on geochemistry which I cannot readily answer or solve, I probably know the people or best route to go to get the information to resolve the situation. I certainly do not want to be caught in the embarassing position of being confronted with geochemical problems concerning your project having never been consulted about them by you.

Discussion will be split up on the basis of the three fundamental aspects of exploration geochemistry:

Sample Collection
Sample Analyses
Management and Interpretation of Geochemical Data

SAMPLE COLLECTION

A) Orientation Surveys

Sample collection is generally a very, if not the most, expensive part of any geochemical program. As such, sample collection must involve more than just grabbing a handful of material, throwing it in a bag and sending it for analysis. Samplers must be trained in proper collection methods and educated as to the reasoning behind using precisely the same sampling technique at each sample site in order to consistently collect identical sample material from one site to the next. Before undertaking a geochemical program, it is essential, in order to gain the best results by the most economic means, to determine the optimum sampling media, sample interval, method of analysis, etc. This is most reliably done by an orientation survey.

Orientation sampling is best described as a series of preliminary experiments aimed at determining the existence and characteristics of anomalies associated with mineralization. This should also include a review of any relevant literature. The information obtained from the sampling and literature review is used to: (1) define background and anomalous geochemical values, (2) define adequate geochemical prospecting methods utilizing the various available sample media and analytical techniques and (3) identify the criteria and factors that influence dispersion and mobility and thus have a bearing on the interpretation of the geochemical data.

Ideally, although this may not be realistically achievable, orientation sampling should be carried out in areas of known but essentially virgin mineralization, thereby eliminating the complicating effects of human activity and contamination. An important criterion is that the orientation study be conducted over mineralization of the type being sought in an area which can be considered geologically and geomorphologically characteristic of the project area to be prospected. The determination of metal values in various sample media from non-mineralized terrain is also an important objective of the orientation survey. This requires that the sampling programs be extended into areas having no known mineralization but which are characterized as closely as possible by the same environmental conditions of geology, geomorphology, climate, vegetation and topography. Combining data from mineralized and unmineralized areas allows more accurate identification of background levels and anomalous values related to mineralization.

The choice of the medium to be used for the orientation sampling and prospecting - soil, stream sediment, water, vegetation, rock, lake sediment, etc. - is a decision that requires a knowledge of the field area, the prospecting problem and previous geochemical work and experience. When the choice of media has been made, a sampling pattern is designed to test the extent and nature of the geochemical dispersion and enable the definition of the optimum physical parameters for sample collection ([redacted]).

Sampling is the foundation of all mineral exploration, whether the samples are initially reconnaissance stream sediments, a few hand-specimens from bedrock outcrops taken for visual examination, or core samples for detailed studies. No matter how sophisticated and precise the

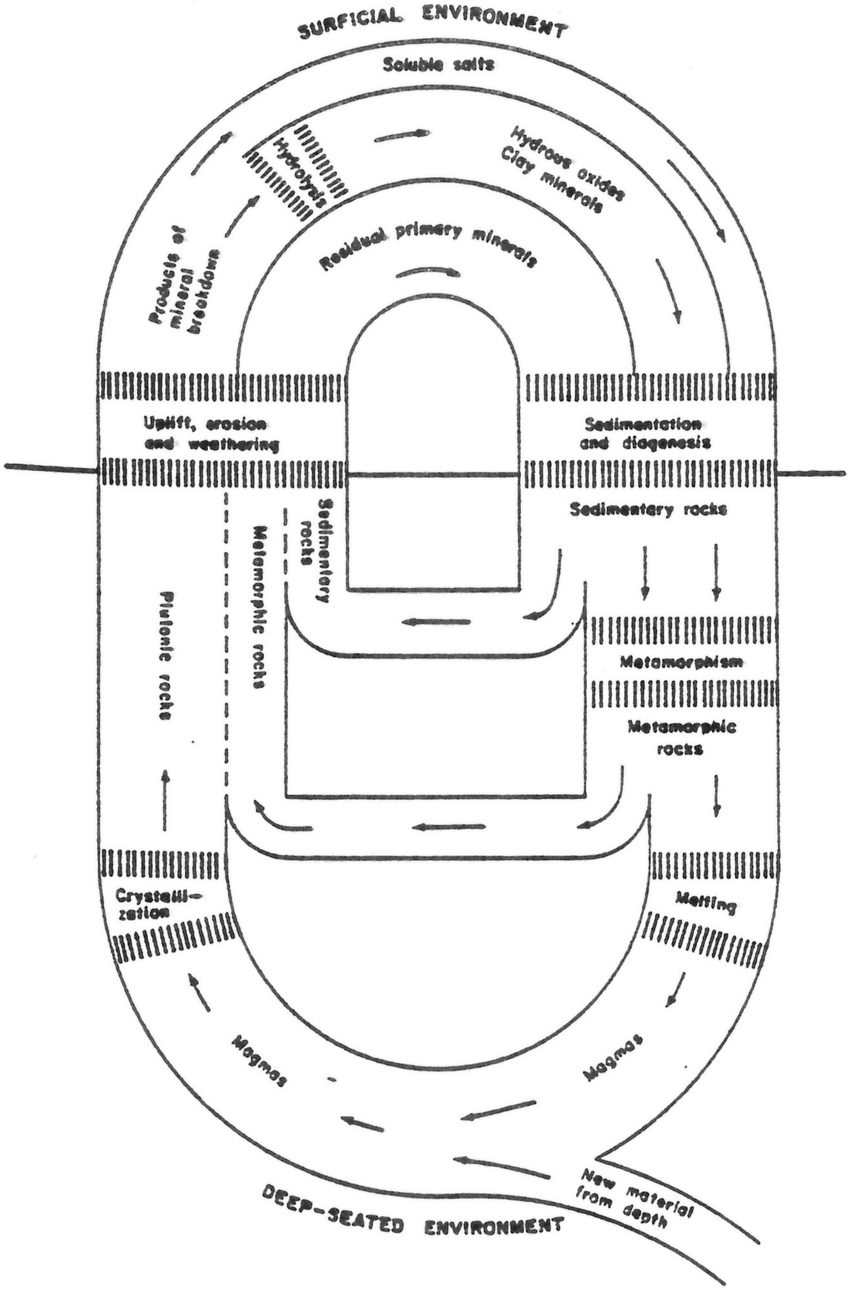


Figure 1. The geochemical cycle

Table 1

Check list of factors to be optimized and evaluated by an orientation survey preparatory to drainage sampling

Sediment	Water
Best indicator elements, including both major and minor constituents of ore	
Optimum material (sediment from seepages, stream channels, flood plain, center-lake, near-shore lake)	Optimum material (ground water vs surface water)
Optimum fraction (size, heavy minerals, organic fraction) Most effective extractant or method of anomaly enhancement Magnitude of contrast of anomaly at source	For ground water, the relation to recharge areas, difference between aquifers, controls on water flow and availability of points where ground water can be sampled. For lake waters, possible variations with depth and type of lake
Length of downstream decay pattern; controls on decay pattern	
Metal content of bank material	pH, Eh, precipitants, absorbents
Background values of indicator elements, range, relation to rock types	
Correlation with Fe-Mn-oxides, organic matter	Relation to total dissolved solids and major elements
Analytical methods (detection limits, precision, accuracy, form of element)	
Seasonal or temporal variations	
Cost of sampling and analytical procedures, and elapsed time for reporting results	

Table 2

Major factors to be evaluated by an orientation survey in residual soil or transported overburden

Optimum contrast between samples at a mineralized zone, representative of that being sought, as compared to a range of background conditions in the survey area, considering the factors below

Determination of the most suitable indicator element or elements, either ore elements or pathfinder elements or both

Nature of overburden:
(a) Residual vs transported, and transport mechanism and direction
(b) Soil profile development
(c) Depth variation of indicator elements
(d) Effects of topography, drainage, vegetation, rock types

Optimum depth of sampling

Optimum size or density fraction (clays, silts, heavy minerals, etc.)

Most suitable analytical procedure:
(a) Extraction method (total, hot-acid extractable, cold-extractable, etc.)
(b) Determination method (detection limit, interferences, cost)

Range of background and intensity of anomaly near mineralization

Shape, extent and homogeneity of anomaly, using preferred method and one or two traverses across mineralization

Reproducibility of sampling and analysis

Possibility of contamination

Table 3

Check list of factors to be determined during biogeochemical orientation surveys

Optimum species based on distribution (must be widespread), contrast of anomalies, homogeneity of anomalies, ease of recognition, ease of sampling and depth of root system

Part of plant to be sampled (twigs, leaves, fruits, bark, wood)

Best indicator element or elements

Effects of aspect (sunlight), drainage, shading, antagonistic effects of other elements

Amount of vegetation needed to give adequate ash

Contamination from dust or other sources

Sampling pattern and interval

Table 4

Check list of factors to be optimized by an orientation survey preparatory to rock sampling

Type of sample (rock, vein material; comparison with soil or drainage samples)

Size and character of sample (single large chunk, many small chips, channel sample, length of drill core)

Best indicator elements (ore element, pathfinder elements, major elements, rare earth elements, element ratios-equations, plots)

Applicability of separated minerals (sulphides, limonite, biotite, calcite, etc.)

Effects of weathering, rock type, hydrothermal alteration and other geological variables on background and contrast of anomalies

Shape, extent and homogeneity of anomalies and reproducibility of anomalies from a single site

Method of sample decomposition and analysis (total analysis, sulphide- or oxide-selective leach, acid digestion)

Sources of contamination (metal from collecting and crushing equipment, dust, drill steel, drill grease or muds, circulating waters, smelter fumes) analytical instrumentation and treatment, statistical studies or financial analysis of mine potential, they do not guarantee profitable or significant outcome if the samples concerned are non-representative or unreliably taken, prepared or subsampled.

pH + Conductivity Meters

B) pH - Eh and Conductivity

Perhaps the most important of all factors governing the solubility, and hence relative mobility and dispersion, of a given element in water is the relationship between pH and Eh.

pH is the concentration of H^+ and OH^- ions in solution expressed as the negative logarithm (to the base 10) of the H^+ ion activity. From this is derived a pH scale ranging from 0 to 14 (acid to alkaline with 7 being neutral).

Eh is a measure of relative oxidizing (removal of e^-) and reducing (gain of e^-) conditions. Positive Eh values indicate oxidizing conditions and negative Eh values indicate reducing conditions relative to the standard hydrogen half cell ($2H^+ + 2e = H_2$, $E^\circ = 0.00$ volts).

Water conductivity may be regarded as a measure of the ionic concentration of the water, or a measure of the total anions (-) and cations (+) in solution.

Data on these three parameters are necessary to determine which elements will exist in solution and be hydromorphically dispersed and which will be precipitated out of solution [redacted]. This information, along with a knowledge of the mineralogy of the mineralization being sought, will aid in determining whether one should be looking for hydromorphic (in solution) or mechanical (clastic) dispersion.

In most cases, pH can be adequately estimated using pH papers which are good enough to detect gross differences (+ 0.5 pH units) in pH. If higher quality (more precise and accurate) pH measurements are required, measurements should be made *in situ* with a field portable meter. Acceptable field pH meters cost about $400 and up.

Precise and accurate conductivity measurements are most practically obtained with a field portable meter. Acceptable conductivity meters cost from $600 upwards.

Eh is a somewhat different problem as reliable data are not as easy to obtain. In most cases in the surficial environment Eh is positive, indicative of relatively oxidizing conditions, and its measurement is really not required. However, this is not always the case with ground waters or drill hole waters. Therefore, Eh measurements should be made on all subsurface waters *in situ*, downhole preferably, as bringing samples to surface results in changes in temperature and pressure conditions and generally produces erroneous Eh data.

Acquisition of pH measurements, using pH papers, should be a routine part of all hydrogeochemical surveys.

Relative Mobilities	Environmental conditions			
	Oxidizing	Acid	Neutral to alkaline	Reducing
Very high	Cl, I, Br S, B	Cl, I, Br S, B	Cl, I, Br S, B Mo, V, U, Se, Re	Cl, I, Br
High	Mo, V, U, Se, Re Ca, Na, Mg, F, Sr, Ra Zn	Mo, V, U, Se, Re Ca, Na, Mg, F. Sr, Ra Zn Cu, Co, Ni, Hg, Ag, Au	Ca, Na, Mg, F, Sr, Ra	Ca, Na, Mg, F, Sr, Ra
Medium	Cu, Co, Ni, Hg, Ag, Au As, Cd	As, Cd	As, Cd	
Low	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Fe, Mn
Very low to immobile	Fe, Mn Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt. Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths Zn Cu, Co, Ni. Hg, Ag, Au	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths S, B Mo, V, U, Se, Re Zn Co, Cu, Ni, Hg, Ag, Au As, Cd Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl

Table 5. Relative mobilities of the elements in the surficial environment

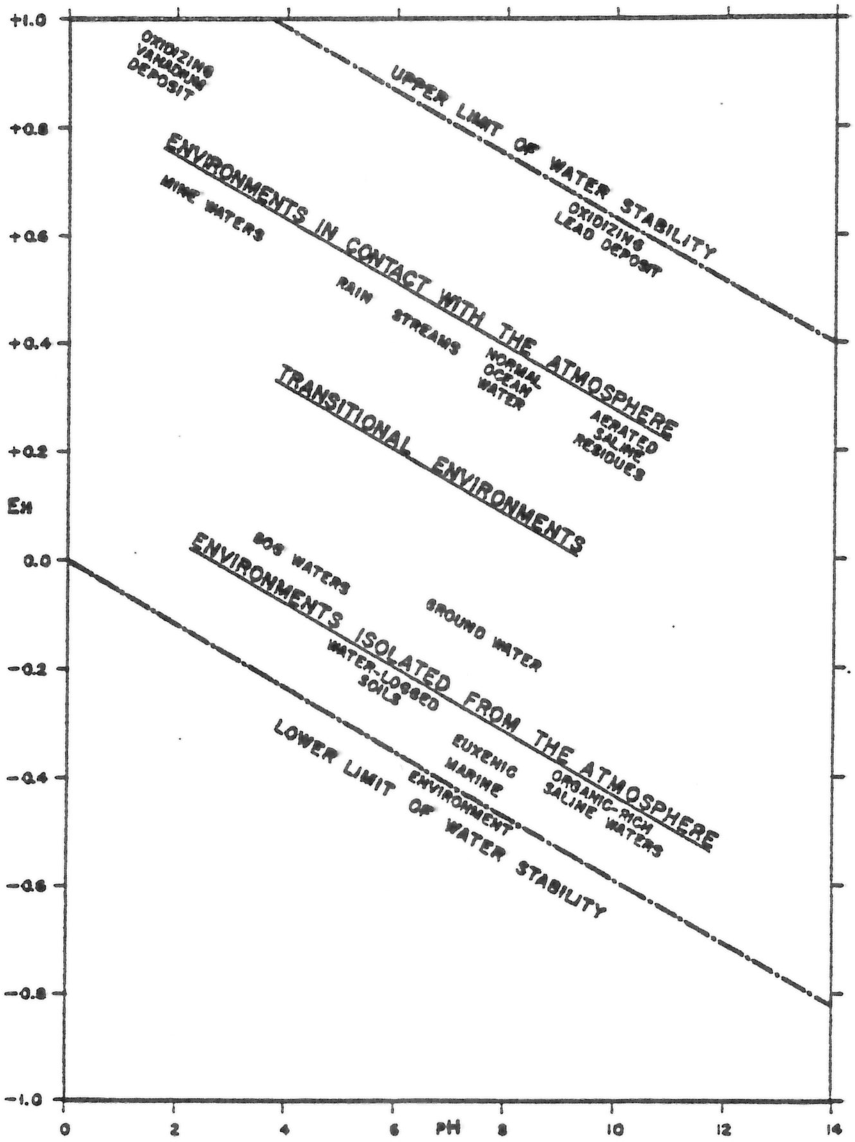


Figure 2. Approximate position of some natural environments as characterized by Eh and pH

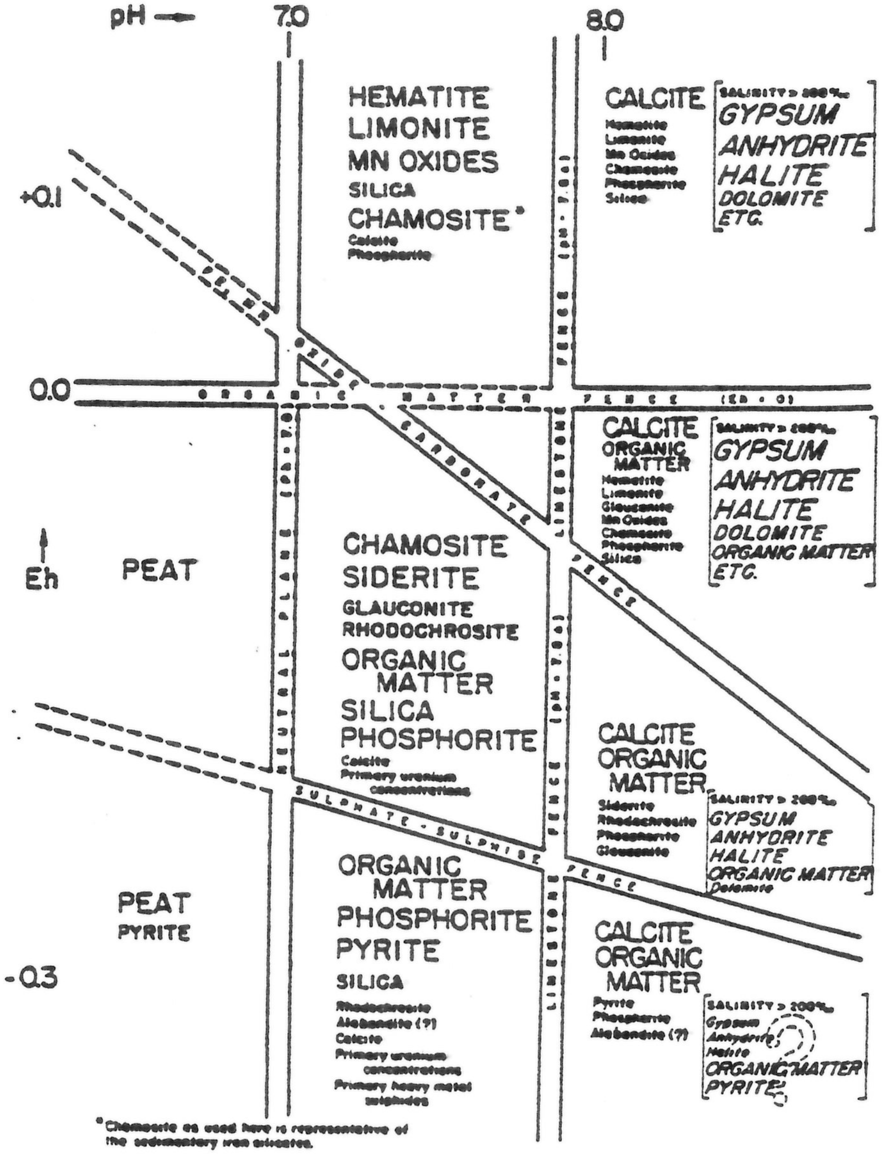


Figure 3. Sedimentary chemical end-member associations relative to environmental limitations imposed by selected Eh and pH values

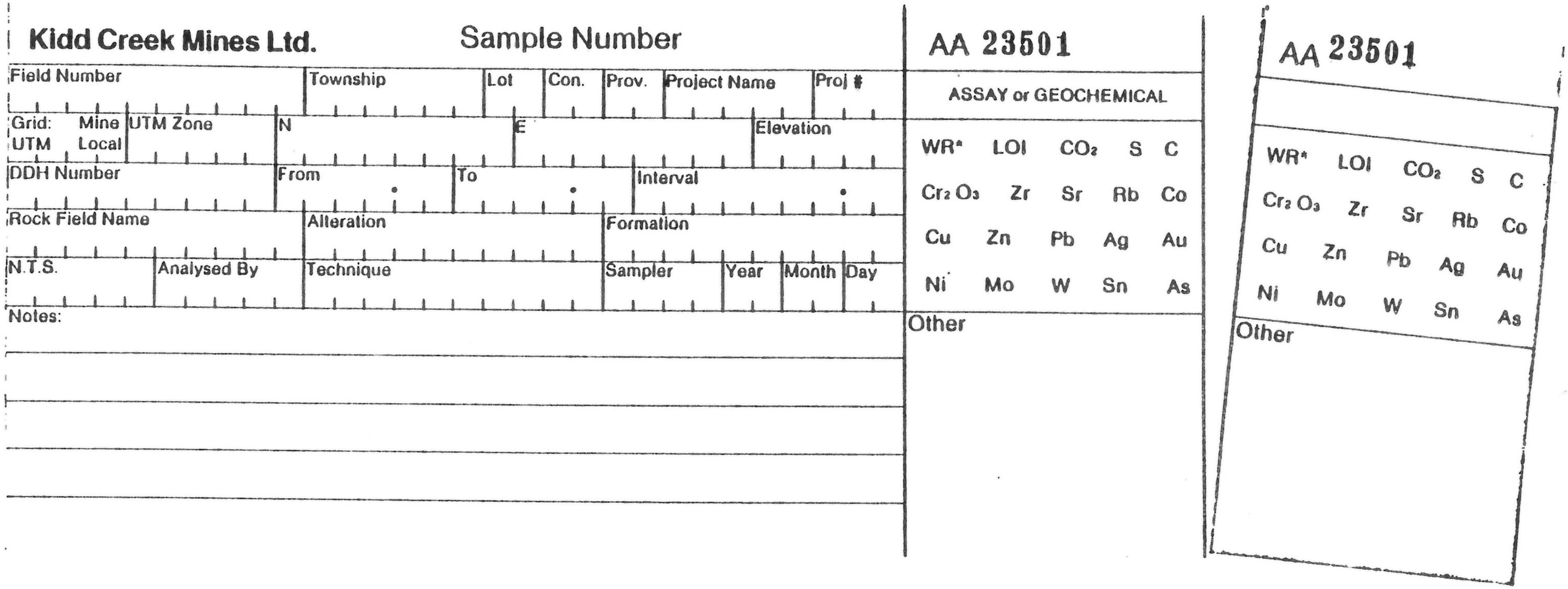
C) Numbering of Geochemical Samples

The present system of numbering samples by Kidd Creek's exploration personnel is somewhat, but not totally, chaotic. With the exception of samples destined for the Whole Rock Data Base (WRDB), which are eventually numbered using the Assay/Geochemical Tag Book sample number (i.e. 2 letters and up to 5 numbers, AA, AB to AZ from 1 to 30000) (Figure 4), each geologist has evolved his own system of numbering samples.

In most instances, various combinations of identifiers for year, project number or name, sampler, sample type and sequential sample number are used. Under the proposed computer-oriented system, this type of information will be included as header data and need not be incorporated into the actual sample number.

Starting in 1983, a rigid 7 character (2 letter, 5 number) system for identifying samples will be instituted across Canada within the Exploration Division. All bedrock samples (i.e. grab, drill core, trench, etc.) whose chemical or other data are destined for the WRDB must be assigned Assay/Geochemical Tag Book numbers (AA to AZ from 1 to 30000). Other types of samples (i.e. soils, overburden, stream/lake sediments and waters, etc.) will use an identical 7 character (2 letter and 5 number (1 to 30000) identification system as outlined in Table 6.

Conformity to this numbering system will allow easy entry of the data into Kidd's geochemical data file structure.



Kidd Creek Mines Ltd. Sample Number

Field Number | Township | Lot | Con. | Prov. | Project Name | Proj #

Grid: UTM | Mine Local | UTM Zone | N | E | Elevation

DDH Number | From | To | Interval

Rock Field Name | Alteration | Formation

N.T.S. | Analysed By | Technique | Sampler | Year | Month | Day

Notes:

AA 23501

ASSAY or GEOCHEMICAL

WR*	LOI	CO$_2$	S	C
Cr$_2$O$_3$	Zr	Sr	Rb	Co
Cu	Zn	Pb	Ag	Au
Ni	Mo	W	Sn	As

Other

AA 23501

WR* LOI CO$_2$ S C
Cr$_2$O$_3$ Zr Sr Rb Co
Cu Zn Pb Ag Au
Ni Mo W Sn As

Other

Figure 4. Assay/Geochemical Tag Book Numbering System

Sample Identifier		Sample Type
AA to AZ	1 to 30000	Whole Rock Data Base (Note PA - published data and TA - old Texasgulf data also used in WRDB)
QA to QZ	1 to 30000	Overburden Drilling Samples
DA to DZ	1 to 30000	Drainage Samples (i.e. stream sediments, waters, panned concentrates, etc.)
SA to SZ	1 to 30000	Soil and Overburden Samples

(AA00001 to AA30000, AB00001 to AB30000 to AZ00001 to AZ30000 allows 780,000 samples to be collected under each code before new letters have to be assigned to a given sample type.)

Table 6. Geochemical Sample Identification System: Kidd Creek Mines Ltd., 1983

D) Identification of Sample Location

Some form of co-ordinates should be assigned to each and every sample collected to enable easy location and plotting of both sample sites and resulting analytical data.

The Universal Transverse Mercator (U.T.M.) Grid System exists on all National Topographic System (N.T.S.) 1:250,000 and 1:50,000 topographic maps. Unfortunately, maps at these scales are not published for all areas of Canada, in particular the northern parts of the provinces and a great deal of both the Yukon and Northwest Territories.

If the U.T.M. grid exists on maps available for your project area, digitizing the sample sites can be done by hand. Using a celluloid roamer, the sample site co-ordinates may be read to an accuracy of 10 or 100 metres respectively on 1:50,000 and 1:250,000 scale maps. The co-ordinates consist of three parts: the Zone (2 digit - Figure 5), Easting (6 digit) and Northing (7 digit) (Figures 6 and 7). Although machine digitizing facilities are available at the mine site in Timmins, they have not been used to any great extent for geochemical data to date. In the future, it is hoped that digitizing will not have to be done by hand. Submitting a sample location map, with accurate U.T.M. co-ordinates specified for all four corners, will allow U.T.M. co-ordinates for all sample locations to be digitized.

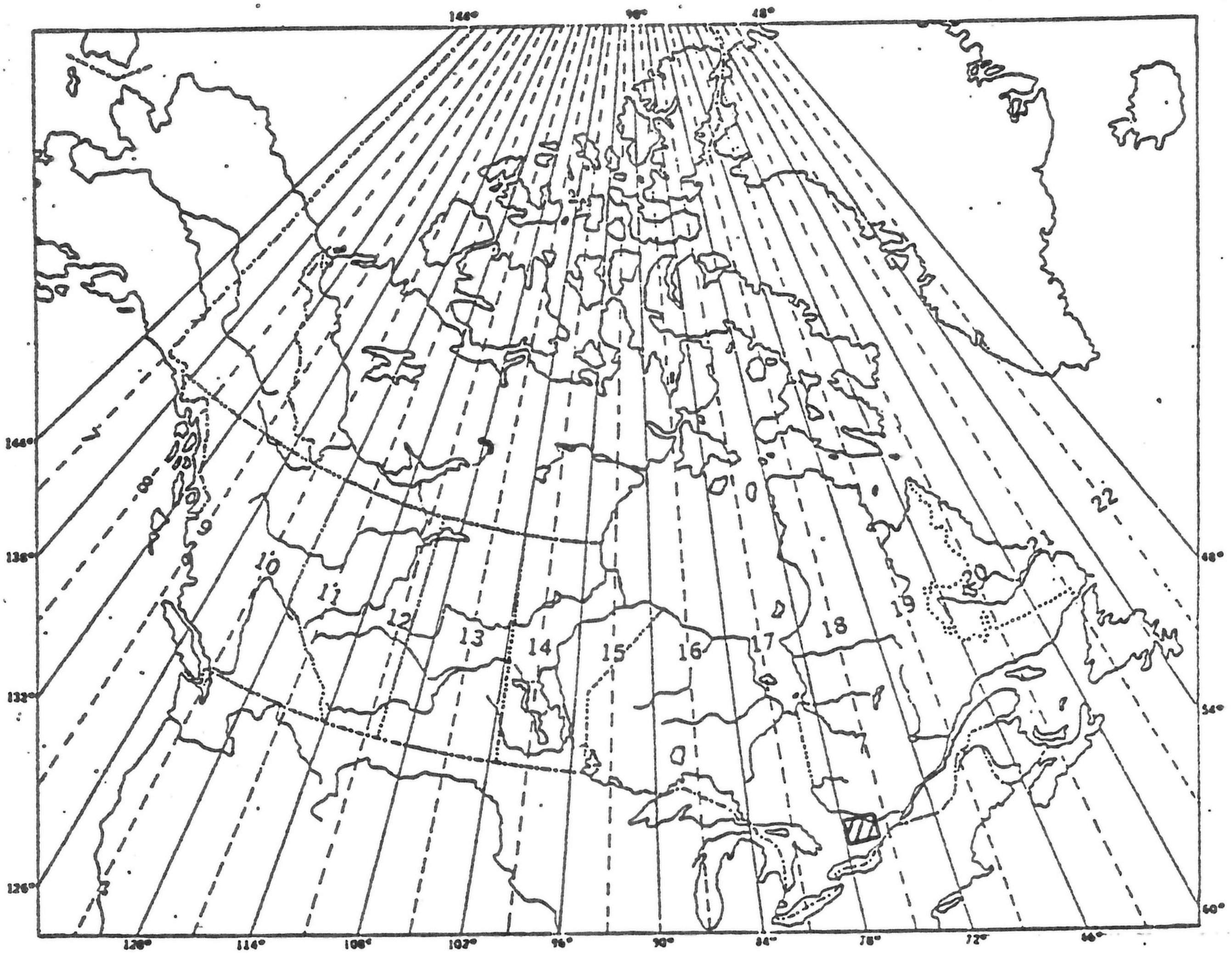
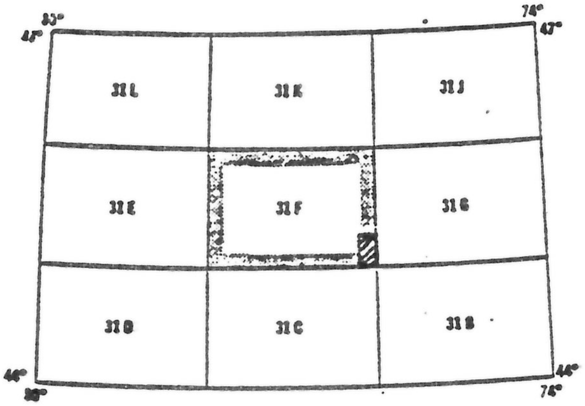
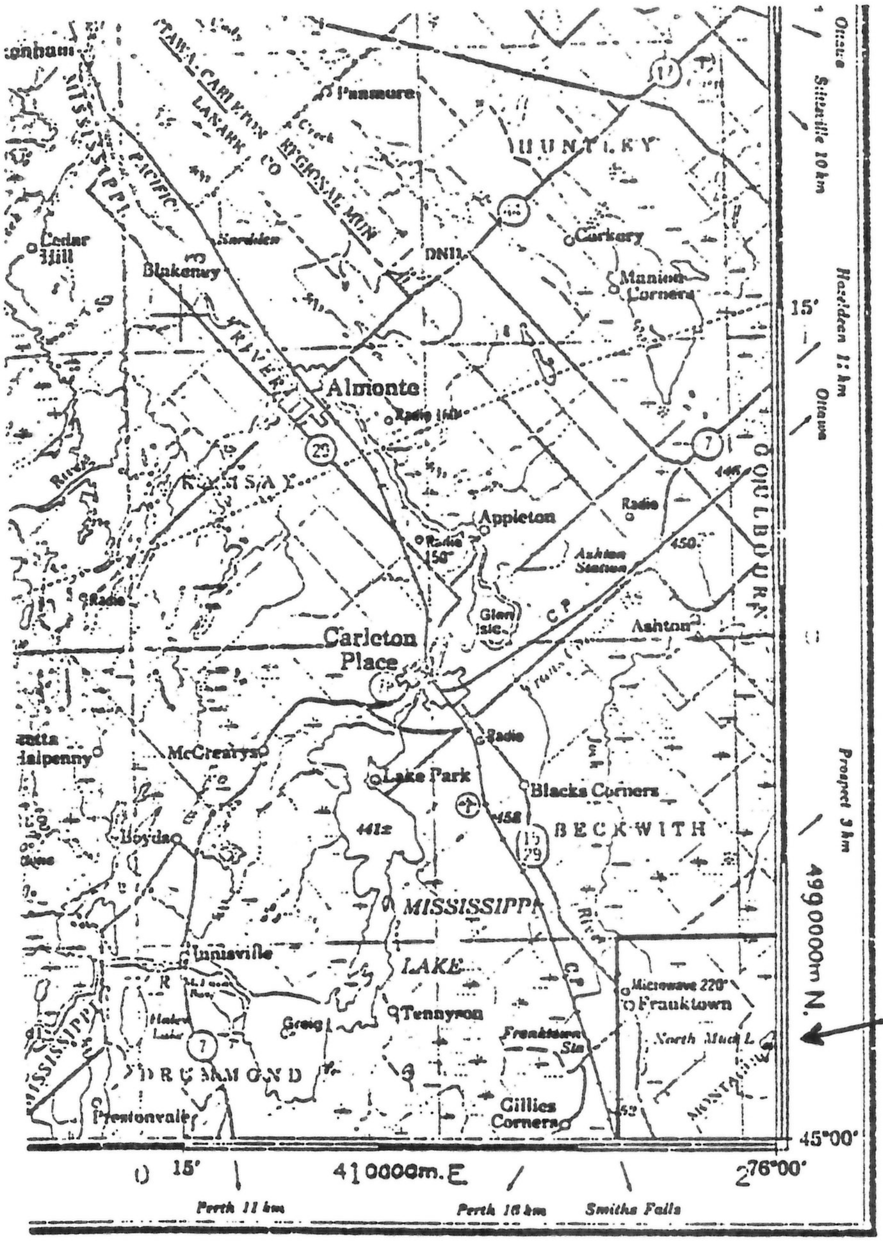


Figure 5. U.T.M. Zones and Central Meridians, Canada
(Location of N.T.S. map sheet 31F given)



Index to adjoining Maps of the National Topographic System

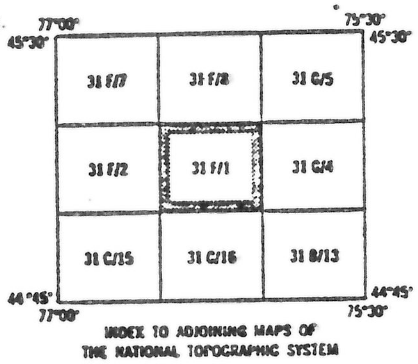


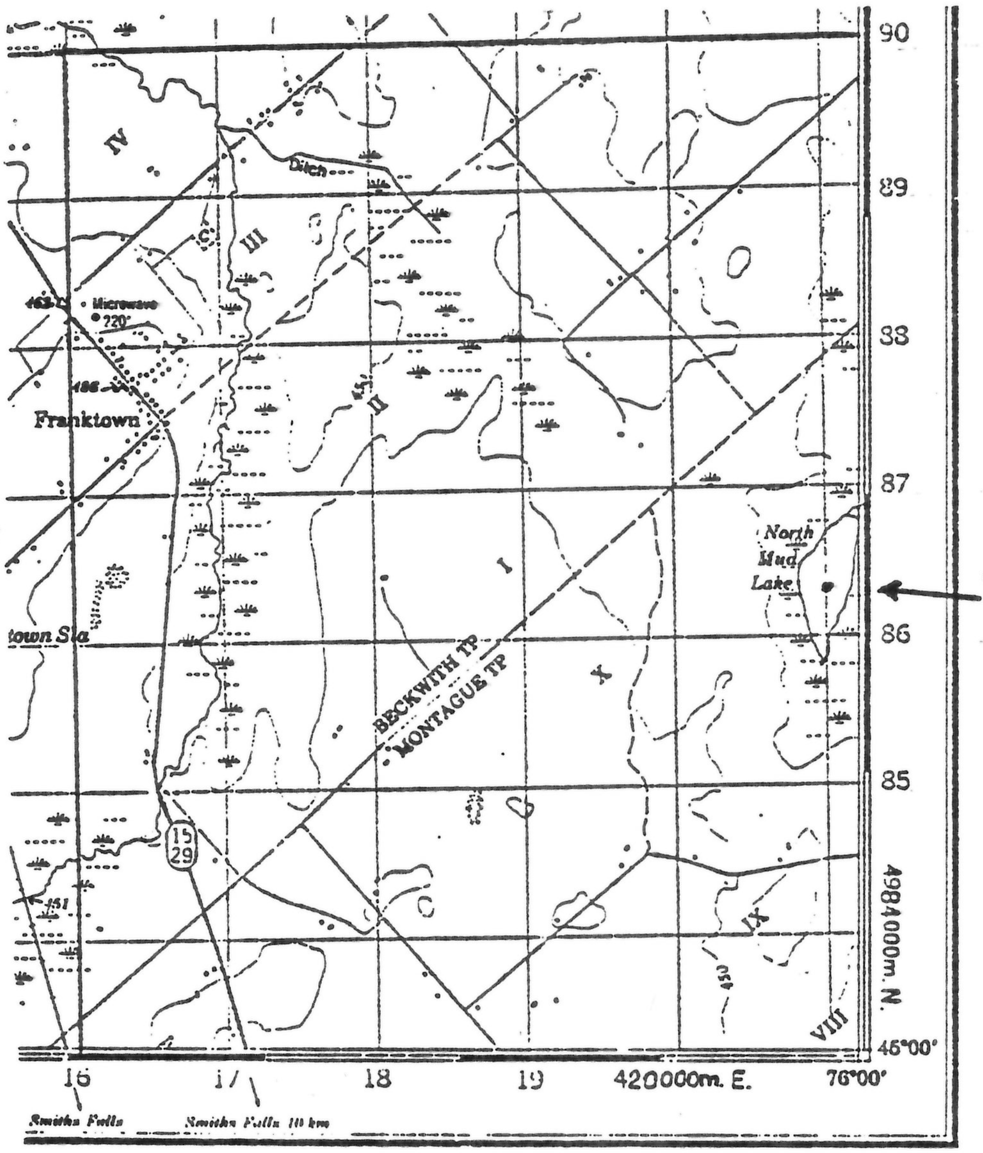
TEN THOUSAND METRE
UNIVERSAL TRANSVERSE MERCATOR GRID
ZONE 18

Lake Sediment
Sample from
North Mud Lake

Zone : 18
Easting : 420900
Northing : 4986300

Figure 6. Pembroke (31F) 1:250,000 topographic map, southeast corner





ONE THOUSAND METRE
UNIVERSAL TRANSVERSE MERCATOR GRID
ZONE 18

Lake Sediment
Sample from
North Mud Lake

Zone : 18
Easting:421000
Northing: 4986350

Figure 7. Carleton Place (31F-01) 1:50,000 topograghic map, southeast corner

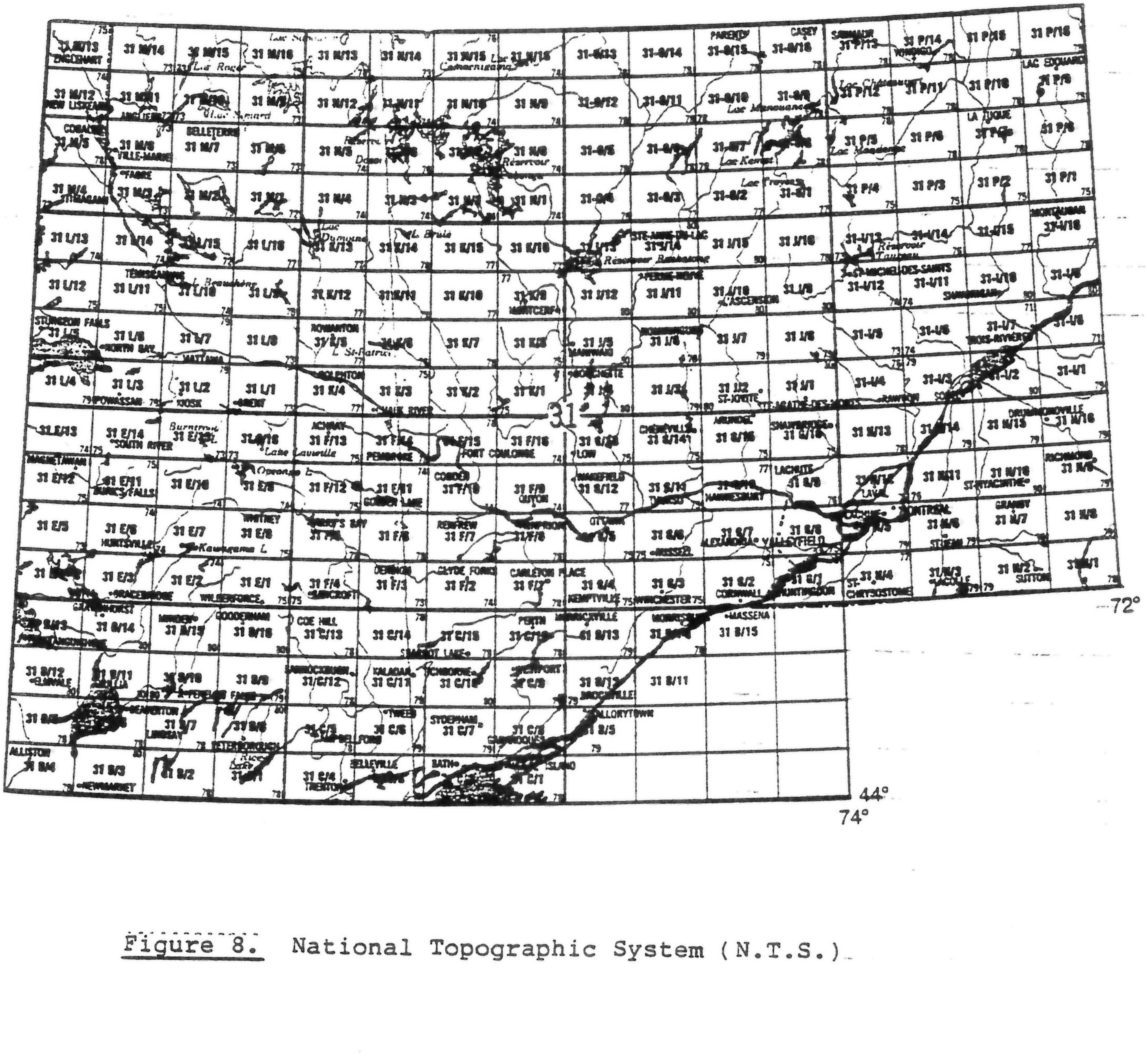


Figure 8. National Topographic System (N.T.S.)

The use of U.T.M. co-ordinates is particularly suited to reconnaissance or semi-detailed sampling programs. For detailed sampling, this system is not adequate. In the case of a detailed gridded soil sampling survey, the U.T.M. co-ordinates of the intersection of the grid baselines should be recorded and then all sample sites referenced to the sampling grid (i.e. 100N, 2000W, etc.). Drill core samples can be located by giving the U.T.M. co-ordinates of the drill hole collar, drill hole information (azimuth, dip and collar elevation) and core interval sampled (i.e. top and bottom of sampled interval) as is done for the WRDB (see Figure 9).

Recording of the National Topographic System (N.T.S.) map sheet number (a seven digit alpha-numeric character) would be an aid to identifying where the samples were collected ([redacted]). The use of N.T.S. notation is also useful in filing, documentation and archiving of data.

E) Field Data Acquisition

Collection of geochemical samples should involve more than simply obtaining consistent sample material from each site. Careful notation of anything which may be of value to the interpretation of the derived chemical data should be routinely recorded by the sample collector.

There exists within the Exploration Division of Kidd Creek Mines Ltd. a critical need for standardization in the collection and reporting of field observational data. All too often, relevant observations are not recorded, only intermittedly recorded or recorded in field notebooks or on sheets of paper (freehand or with a fixed format) which are never actually used during the interpretation of the chemical data. If a thorough interpretation of the data is to be undertaken, certain parameters, which could affect the chemistry of the particular media sampled, must be observed and systematically recorded. If those parameters are to be consistently and rapidly recorded by many sampling crews, it is necessary to formalize the note taking. Also, the acquisition of field and analytical data in an organized fashion allows systematic computer storage. The data will thereby have some continuing value past the immediate project and can be returned to or compiled with other data at a later date.

1) Whole Rock Data Base/Header Data

Basically, the only organized system for computer-based acquisition and management of geochemical data currently in existence within the Exploration Division is the Whole Rock Data Base (WRDB).

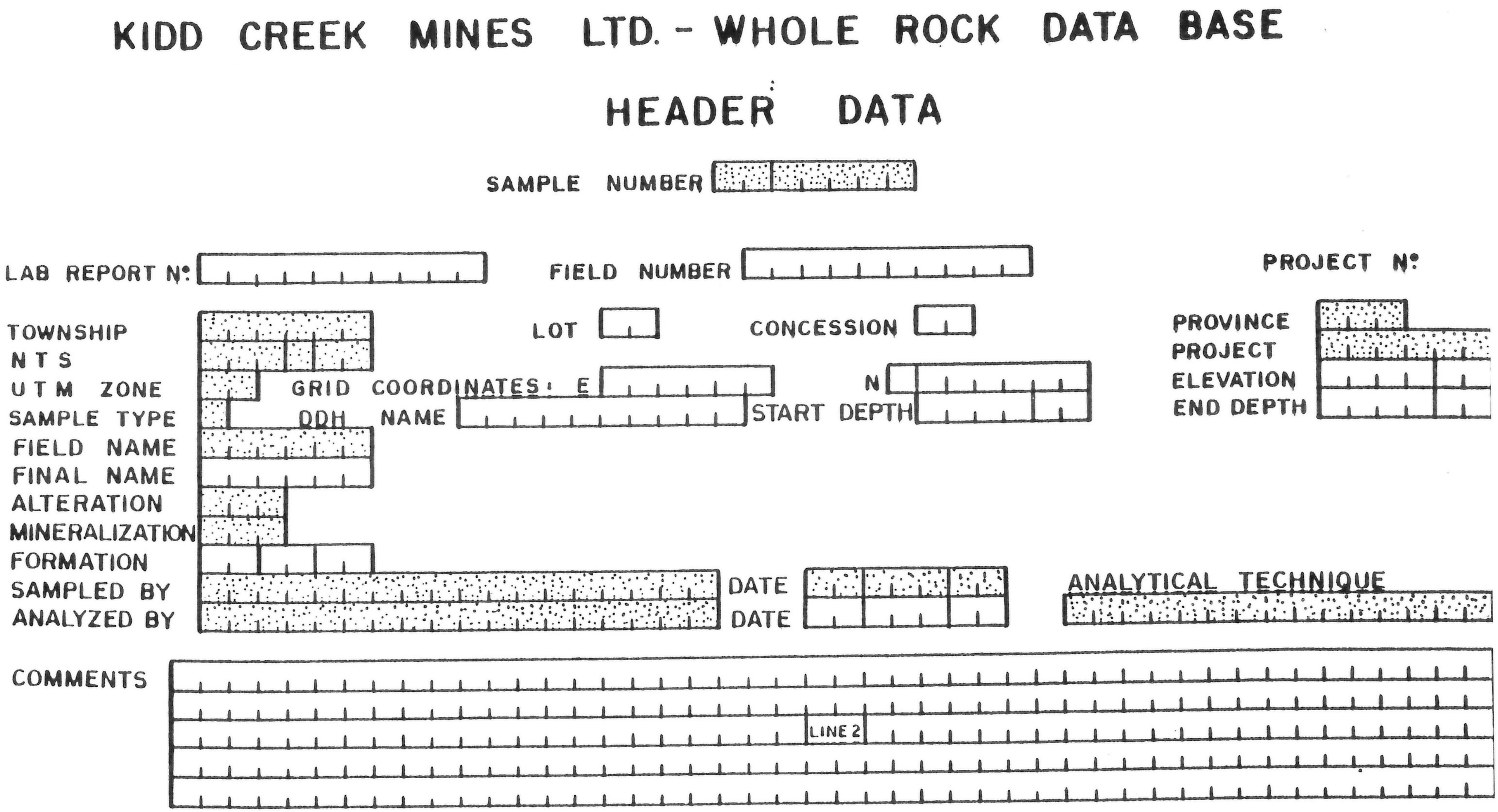
The Whole Rock Data Base is designed as a flexible system of computer programs for the storage, retrieval and manipulation of large numbers of whole rock analyses. This data base has been tailored towards exploration for massive sulphide and gold deposits in Archean greenstone belts, but can be easily adapted for other objectives by adding to existing codes.

The fundamental information stored - the data record - is composed of two parts, the analyses and the header data. Normally, the analyses will be entered into the data base directly from tapes supplied by the analytical laboratory. The header data that describes the sample must be supplied by the geologist [redacted].

The Whole Rock Data Base Users' Manual (Tony Green, September 1982) lists the codes used for all the coded variables noted on the "Header Data" form ([redacted].

Abbreviated outlines of the codes used for "Field Name", "Alteration" and "Mineralization" in the example illustrated in Figure 10 are given in [redacted] respectively. The data base system will be no better than the data it contains, so only reliable, complete and carefully checked data should be entered into the system.

The Whole Rock Data Base has been designed to permit revision of the sample descriptions and to provide access to many forms of data manipulation. The current users' manual (Tony Green, September 1982) describes data input techniques, screening routines and report programs now available. Anyone using the system should refer to the users' manual for details on the codes used, etc. Additions and modifications to most codes can be readily accommodated by the data base, so these should be recommended whenever the present codes do not fit your requirements.



KIDD CREEK MINES LTD. - WHOLE ROCK DATA BASE

HEADER DATA

SAMPLE NUMBER

LAB REPORT N°

FIELD NUMBER

PROJECT N°

TOWNSHIP

N T S

U T M ZONE

SAMPLE TYPE

FIELD NAME

FINAL NAME

ALTERATION

MINERALIZATION

FORMATION

SAMPLED BY

ANALYZED BY

LOT

CONCESSION

GRID COORDINATES: E

N

DDH NAME

START DEPTH

PROVINCE

PROJECT

ELEVATION

END DEPTH

DATE

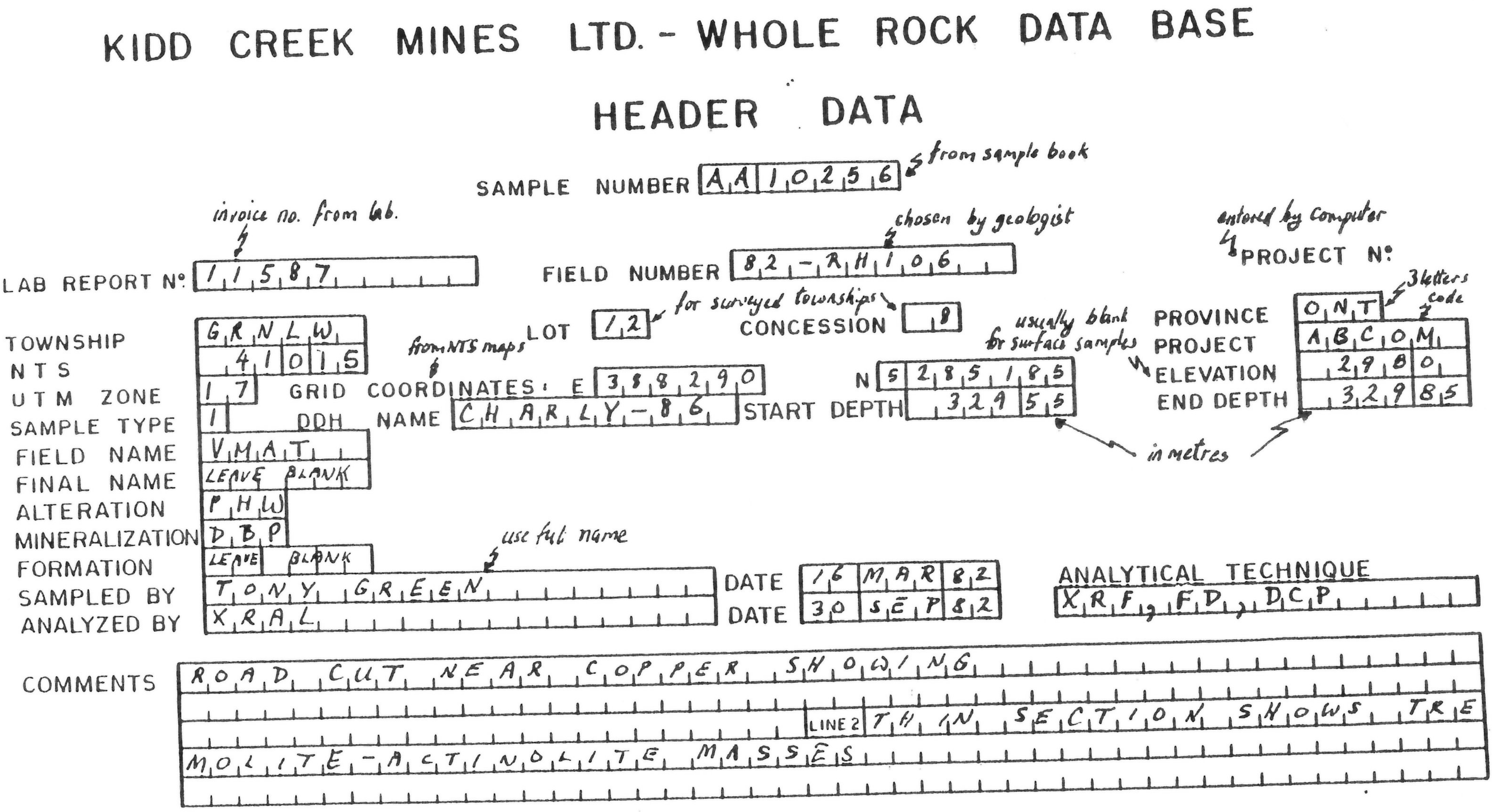
DATE

ANALYTICAL TECHNIQUE

COMMENTS

LINE 2

Figure 9. Whole Rock Data Base - Header Data (Header data items that must be supplied for every sample are shaded)



KIDD CREEK MINES LTD. - WHOLE ROCK DATA BASE

HEADER DATA

SAMPLE NUMBER AA10256 ← from sample book

LAB REPORT Nº 11587 ← invoice no. from lab.

FIELD NUMBER 82-RH106 ← chosen by geologist

PROJECT Nº ← entered by computer

TOWNSHIP GRNLW

NTS 41015 ← from NTS maps

LOT 12 ← for surveyed townships → CONCESSION 8

PROVINCE ONT ← 3 letters code

PROJECT ABCOM

UTM ZONE 17 GRID COORDINATES: E 388290 N 5285185

ELEVATION 2980 ← usually blank for surface samples

SAMPLE TYPE 1 DDH NAME CHARLY-86 START DEPTH 32955 END DEPTH 32985 ← in metres

FIELD NAME VMAT

FINAL NAME LEAVE BLANK

ALTERATION PHW

MINERALIZATION DBP

FORMATION LEAVE BLANK

SAMPLED BY TONY GREEN ← use full name DATE 16 MAR 82

ANALYZED BY XRAL DATE 30 SEP 82

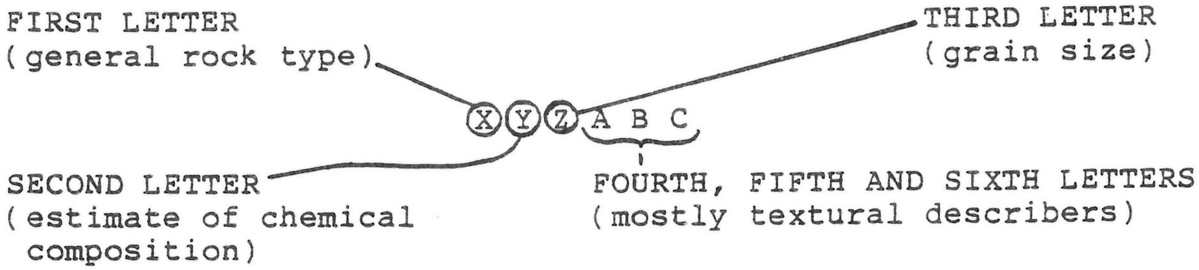
ANALYTICAL TECHNIQUE XRF, FD, DCP

COMMENTS ROAD CUT NEAR COPPER SHOWING

LINE 2 THIN SECTION SHOWS TREMOLITE-ACTINOLITE MASSES

Figure 10. Example of coded Header Data for the Whole Rock Data Base

Figure 11. Explanation of Field Rock Name Codes
Whole Rock Data Base (Specific to Figure 10)



X, Y and Z must be entered. A, B and C are optional. None, one, two or three may be entered, but they should be filled in from left to right.

Example Figure 10. Field Name V M A T _ _

'X' FIRST LETTER (Outcrop scale observation)

I	Igneous (unspecified, unidentifiable as definitely volcanic or plutonic)
P.	Plutonic (intrusive)
V	Volcanic (product of lava flowing)
T	Volcaniclastic (product of movement of solidified lava - airfall, mass transport)
S	Sedimentary
M	Metamorphic (use only where primary nature of rock cannot be deduced)
F	Vein material
O	Other (massive sulphides, skarns, etc.)

'Y' SECOND LETTER (For I,P,V,T,M, this is an estimate of the chemical composition of the actual sample, not of outcrop it comes from.)

U	Ultramafic	(90 volume % mafic minerals)
M	Mafic	(50 volume % mafic minerals)
I	Intermediate	(transitional between mafic and felsic)
F	Felsic	(rich in light minerals - feldspar and and feldspathoid, muscovite and silica)
A	Alkalic	(rich in sodium and/or potassium)
O	Other	

'Z' THIRD LETTER (Grain Size)

	Igneous Rocks (I, P or V)	Metamorphic Rocks (M)
A	1 mm	fine
B	1-5 mm	medium
C	5 mm	coarse

Figure 11. Explanation of Field Rock Name Codes
Whole Rock Data Base (continued)

'A B C' FOURTH, FIFTH AND SIXTH LETTERS - IGNEOUS ROCKS (I and/or V

A	Aphyric (lacks phenocrysts)
M	Massive (structural sense only)
G	Glomeroporphyritic (contains irregular clusters of felsic crystals)
E	Equigranular (even-grained)
F	Feldspar porphyritic (large feldspar crystals in finer matrix)
Y	Amygdaloidal (contains amygdules or vugs)
H	Hyaloclastitic (formed by shattering of lava or magma by water, ice or wet sediment)
I	In situ brecciated (brecciation into jigsaw fragments - non-genetic)
Z	Polysutured (polyhedral jointing as in spinifex - poor komatiitic flows)
K	Skeletal (crystals with incomplete filling of crystal faces, e.g. plagioclase or chromite)
L	Flow banded or flow laminated (banding due to movement of lava)
W	Mafic porphyritic (large, mafic crystals in finer matrix
N	Gneissic (foliation with bands of alternate flaky and non-oriented minerals)
B	Autobrecciated (either agmatite, flow breccia or pillow breccia, etc.)
Q	Quartz porphyritic (large quartz crystals in finer matrix)
U	Sperulitic (crystalline aggregates with radial internal structure in siliceous rocks)
T	Tectonized (rock is notably foliated or sheared)
D	Quartz and feldspar porphyritic
V	Variolitic (spherical clusters of felsic crystals in mafic igneous rock)
O	Olivine spinifex (skeletal olivine blades in komatiite)
X	Pyroxene spinifex (skeletal, oriented pyroxene crystals in komatiite)
C	Pillow core (where only core is sampled)
R	Pillow rim (where only rim is sampled)
P	Pillowed (sample from pillowed outcrop)
J	Cumulate (accumulated crystals, commonly in layers)
*	Look at comments file
-	No comment

ALTERATION CODE

FIRST LETTER (type of alteration)

P	Pervasive
F	Fracture-controlled
X	In situ brecciation
Q	Silica dumping
C	Carbonate dumping
O	Centred on amydules
S	Spots

SECOND LETTER (facies of alteration)

Q	Silicification
S	Sericitization
U	Fuchsitization
H	Chloritization
E	Epidotization
C	Carbonatization
F	Hematitization
B	Bleaching
A	Alkalic
G	Graphitic or free carbon zones
T	Talc
L	Talc-carbonate
R	Serpentine
*	Look at comments

THIRD LETTER (strength of alteration)

W	Weak
M	Moderate
S	Strong
-	No comment
*	Look at comments

Figure 12. Explanation of Alteration Codes
Whole Rock Data Base

MINERALIZATION CODE

FIRST LETTER (type of alteration)

D	Disseminated and blebs
S	Stringers
B	Bedded, laminated
V	In veins
N	Nodules, concretions
A	Nil
M	Massive

SECOND LETTER (estimated total quantity of mineralization)

A	Nil
B	Less than 1%
C	1-5%
D	5-20%
E	20-50%
F	50-100%

THIRD LETTER (mineralization type)

A	Arsenopyrite
B	Sphalerite
C	Chalcopyrite
D	Pyrrhotite plus chalcopyrite
G	Visible gold present
H	Sphalerite plus pyrite
I	Sphalerite plus chalcopyrite
J	Pyrite and visible gold
K	Sphalerite plus pyrite
L	Galena
M	Molybdenite
N	Molybdenite plus scheelite
O	Pyrrhotite
P	Pyrite
Z	Scheelite
T	Tellurides
Y	Pyrite plus chalcopyrite
*	Look at comments files
-	No comment

Figure 13. Explanation of Mineralization Codes
Whole Rock Data Base

2) Geochemical Data Base/Field Cards

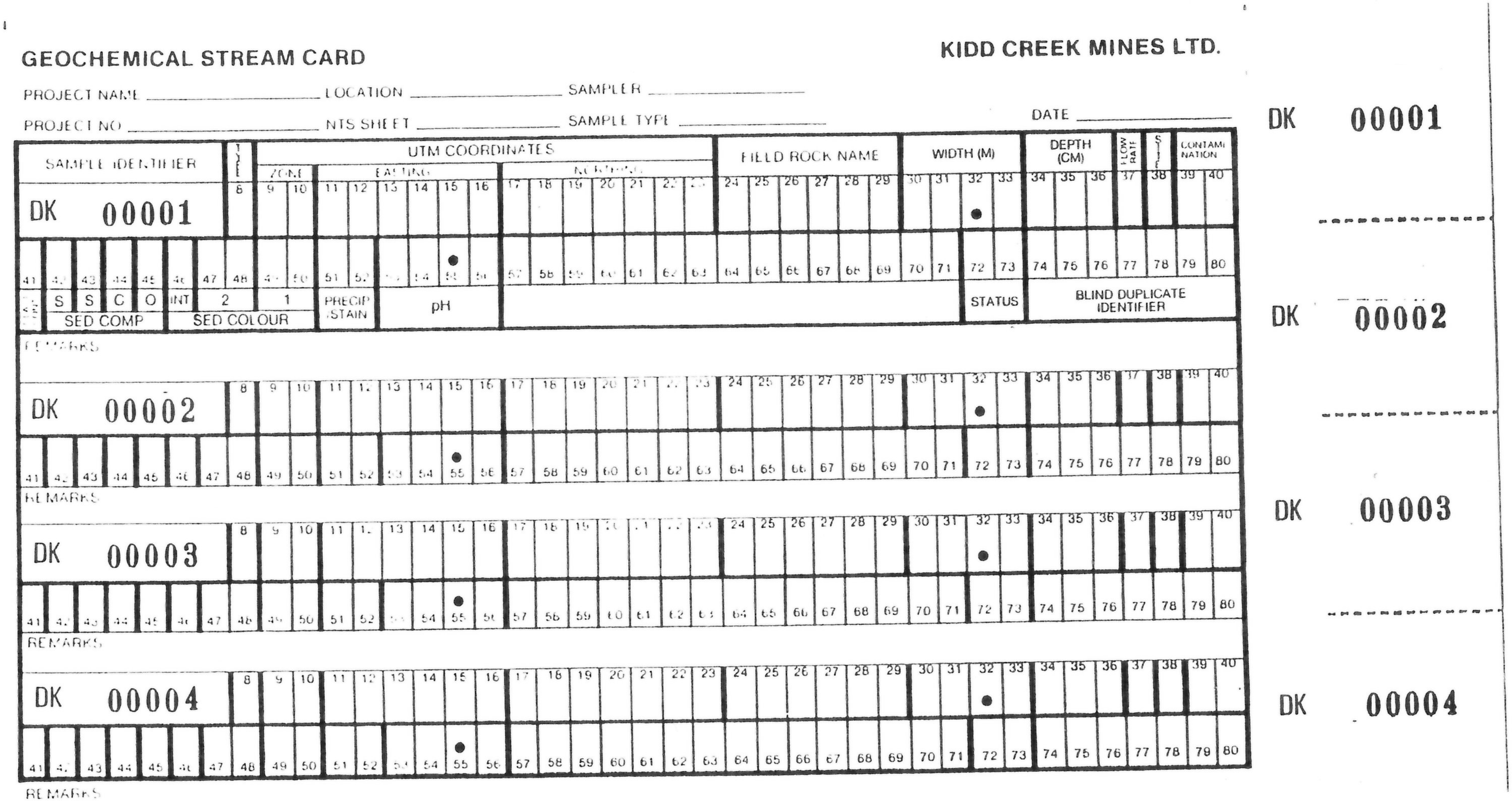
The number of samples (i.e. soils, overburden, stream sediments and waters, lake sediments and waters, etc.) being collected by Kidd necessitates that field notes and analytical results be acquired and systematically stored if anything, but the most superficial interpretation of the data is to be carried out within a reasonable time span, and if the data are to have lasting value. Routine use of computer-oriented field cards and computer technology for the manipulation of geochemical data is beyond being a necessity within Kidd.

The geologist or geochemist managing a sampling program must ensure the systematic recording of all features potentially relevant to the data interpretation. Systematic recording of sample site co-ordinates by hand-digitizing with a roamer or by supplying a sample location map for machine-digitizing, allows the rapid machine plotting of field observations and analytical results. The time and cost saved through plotting by machine, rather than by hand, can alone justify the use of computer technology. Furthermore, once this stage has been reached, a small additional expenditure will allow for a more thorough investigation of the data.

In order to systematize field data collection and ensure consistent recording of observations and measurements, fixed formated field cards (for mandatory data) and with a degree of flexibility (for optional data), will be instituted within Kidd. Prototype field cards were tested in 1983. The Geochemical Stream Card (Figure 14) and Geochemical Soil/Overburden Card (Figure 15) were amended, finalized and printed in 1984 for use in all future geochemical surveys. The Geochemical Free Format Card (Figure 16) and Overburden Drill Hole Log (Figure 17) are still under development.

Field card variables will each be identified by a "Keyword" (i.e. SAMPLE IDENTIFIER, UTM COORDINATES, GRID LINE, DEPTH, SLOPE, SOIL HORIZON, COLOUR, PH, etc.). Variables in common with the WRDB will maintain the codes used in the WRDB (i.e. FIELD ROCK NAME, MINERALIZATION, etc.). All "Keywords" will be included in a dictionary/glossary with definitions and method for recording them on the field cards detailed (Figure 18, 19 and 20). As a result, any given variable (i.e. COLOUR, FIELD ROCK NAME, etc.) will be recorded in exactly the same manner on every type of field card used. As the system develops, additions and changes will undoubtedly be required, necessitating a constant updating of the "Keyword" dictionary/glossary.

As a closing comment on sample collection, it should be noted that incorrect sampling, including improper or noncollection of pertinent field observations or chemical (pH, conductivity) data, is perhaps the major source of error in exploration geochemistry. Inadequacies in the sampling program invariably impose limits on the interpretation of the data.



GEOCHEMICAL STREAM CARD

KIDD CREEK MINES LTD.

PROJECT NAME ______ LOCATION ______ SAMPLER ______

PROJECT NO ______ NTS SHEET ______ SAMPLE TYPE ______ DATE ______

SAMPLE IDENTIFIER	TYPE	UTM COORDINATES			FIELD ROCK NAME	WIDTH (M)	DEPTH (CM)	FLOW RATE	SILT	CONTAMINATION
		ZONE	EASTING	NORTHING						
DK 00001	8	9 10	11 12 13 14 15 16	17 18 19 20 21 22 23	24 25 26 27 28 29	30 31 32 ● 33	34 35 36	37	38	39 40

41 42 43 44 45 46	47 48	49 50	51 52	53 54 55 ● 56	57 58 59 60 61 62 63 64 65 66 67 68 69 70 71	72 73	74 75 76 77 78 79 80
S S C O INT	2 1		PRECIP /STAIN	pH		STATUS	BLIND DUPLICATE IDENTIFIER
SED COMP	SED COLOUR						

REMARKS

DK 00002

REMARKS

DK 00003

REMARKS

DK 00004

REMARKS

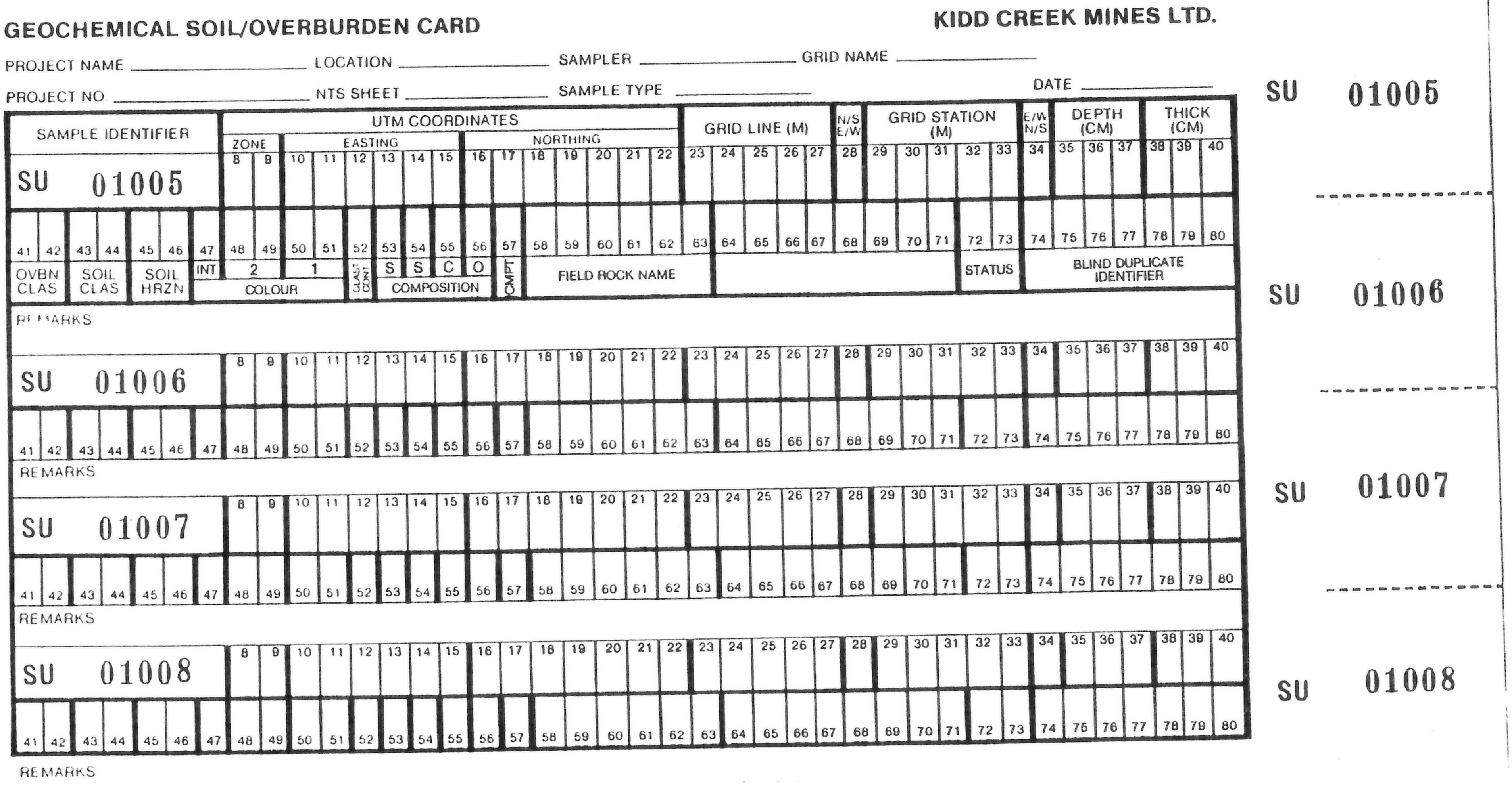
DK 00001

DK 00002

DK 00003

DK 00004

Figure 14. Geochemical Stream Card



GEOCHEMICAL SOIL/OVERBURDEN CARD

KIDD CREEK MINES LTD.

PROJECT NAME ____ LOCATION ____ SAMPLER ____ GRID NAME ____

PROJECT NO ____ NTS SHEET ____ SAMPLE TYPE ____ DATE ____

SAMPLE IDENTIFIER	UTM COORDINATES: ZONE	EASTING	NORTHING	GRID LINE (M)	N/S E/W	GRID STATION (M)	E/W N/S	DEPTH (CM)	THICK (CM)
SU 01005	8 9	10 11 12 13 14 15	16 17 18 19 20 21 22	23 24 25 26 27	28	29 30 31 32 33	34	35 36 37	38 39 40

OVBN CLAS	SOIL CLAS	SOIL HRZN	INT	COLOUR		COMPOSITION	CMPT	FIELD ROCK NAME		STATUS	BLIND DUPLICATE IDENTIFIER
41 42	43 44	45 46	47	48 49 (2) 50 51 (1)	52 (37 38)	53 S 54 S 55 C 56 O	57	58 59 60 61 62	63 64 65 66 67 68 69 70 71	72 73	74 75 76 77 78 79 80

REMARKS

SU 01006

8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

REMARKS

SU 01007

8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

REMARKS

SU 01008

8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

REMARKS

SU 01005

SU 01006

SU 01007

SU 01008

Figure 15. Geochemical Soil/Overburden Card

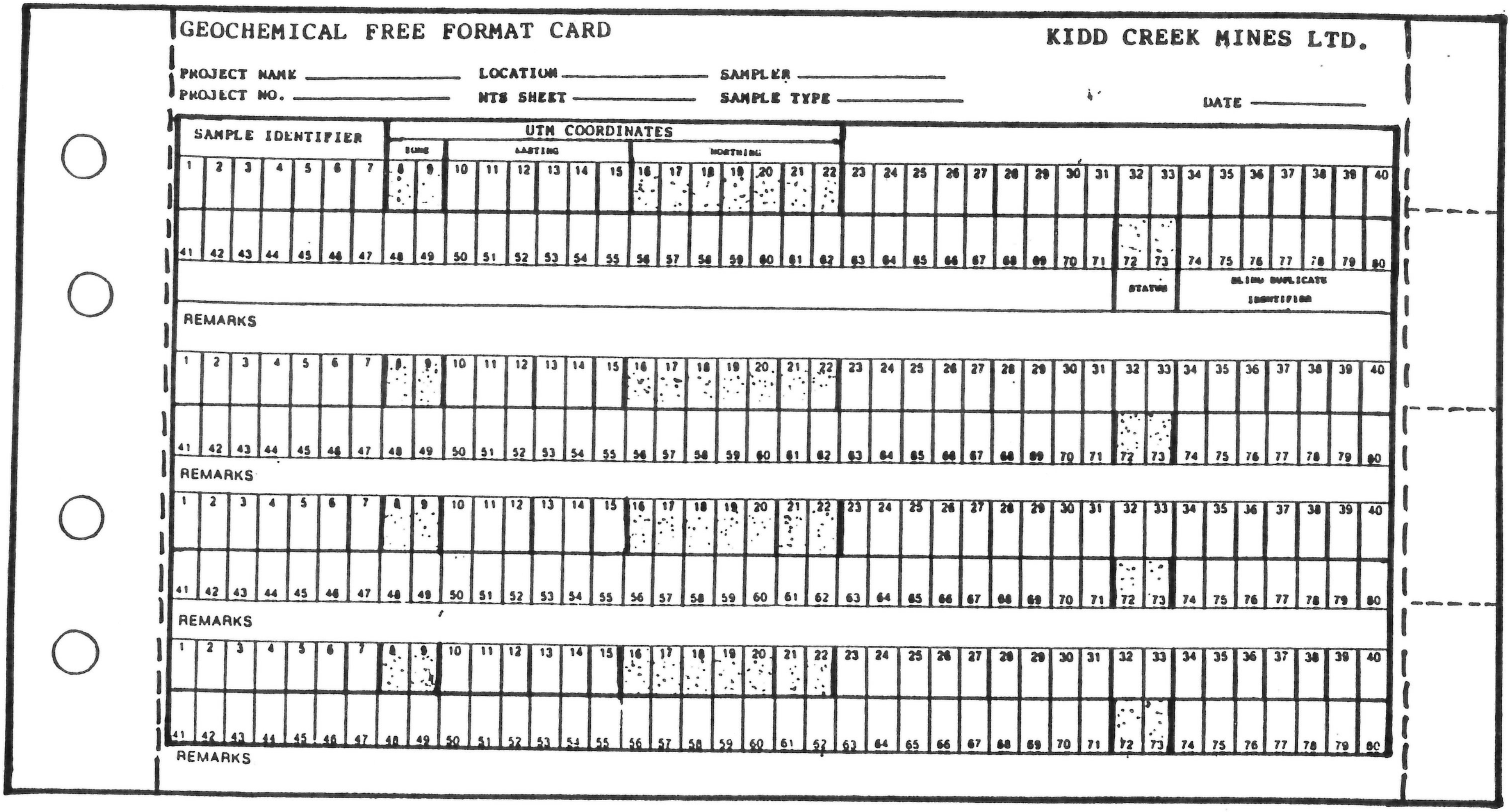
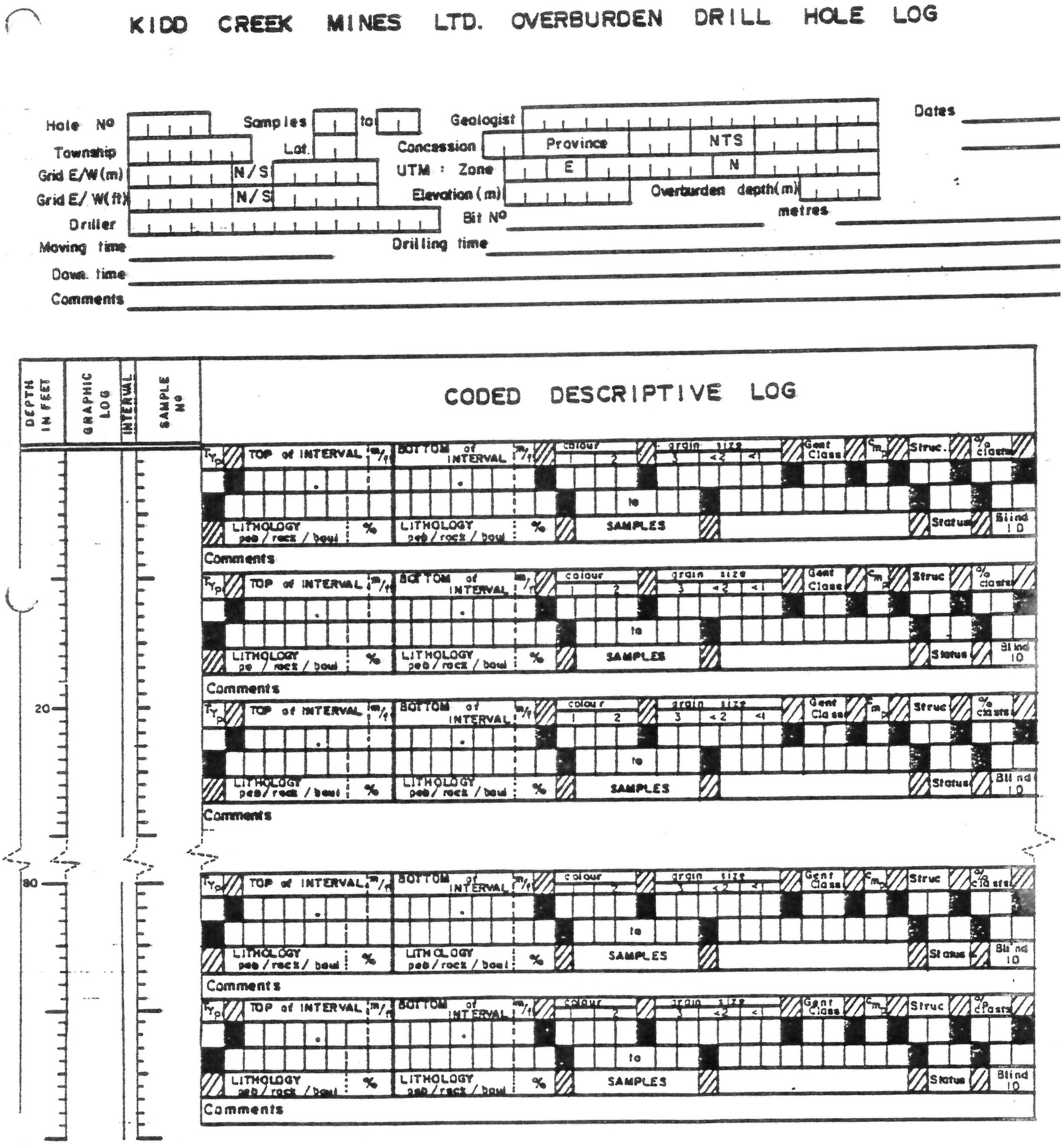


Figure 16. Geochemical Free Format Card



KIDD CREEK MINES LTD. OVERBURDEN DRILL HOLE LOG

Hole No | Samples | to | Geologist | Dates

Township | Lot. | Concession | Province | NTS

Grid E/W(m) | N/S | UTM : Zone | E | N

Grid E/W(ft) | N/S | Elevation (m) | Overburden depth(m)

Driller | Bit No | metres

Moving time | Drilling time

Down time

Comments

DEPTH IN FEET | GRAPHIC LOG | INTERVAL | SAMPLE No

CODED DESCRIPTIVE LOG

Typ | TOP of INTERVAL m/ft | BOTTOM of INTERVAL m/ft | colour 1 2 | grain size 3 <2 <1 | Genl Class | Cmp | Struc. | % clasts

to

LITHOLOGY peb / rock / boul % | LITHOLOGY peb / rock / boul % | SAMPLES | Status | Blind ID

Comments

Typ | TOP of INTERVAL m/ft | BOTTOM of INTERVAL m/ft | colour 1 2 | grain size 3 <2 <1 | Genl Class | Cmp | Struc | % clasts

to

LITHOLOGY pe / rock / boul % | LITHOLOGY peb / rock / boul % | SAMPLES | Status | Blind ID

Comments

20

Typ | TOP of INTERVAL m/ft | BOTTOM of INTERVAL m/ft | colour 1 2 | grain size 3 <2 <1 | Genl Class | Cmp | Struc | % clasts

to

LITHOLOGY peb / rock / boul % | LITHOLOGY peb / rock / boul % | SAMPLES | Status | Blind ID

Comments

80

Typ | TOP of INTERVAL m/ft | BOTTOM of INTERVAL m/ft | colour 1 2 | grain size 3 <2 <1 | Genl Class | Cmp | Struc | % clasts

to

LITHOLOGY peb / rock / boul % | LITHOLOGY peb / rock / boul % | SAMPLES | Status | Blind ID

Comments

Typ | TOP of INTERVAL m/ft | BOTTOM of INTERVAL m/ft | colour 1 2 | grain size 3 <2 <1 | Genl Class | Cmp | Struc | % clasts

to

LITHOLOGY peb / rock / boul % | LITHOLOGY peb / rock / boul % | SAMPLES | Status | Blind ID

Comments

Figure 17. Overburden Drill Hole Log

BLIND DUPLICATE IDENTIFIER
BOTTOM OF INTERVAL
CLAST CONTENT
COLOUR
COLOUR INTENSITY
COMPACTION
COMPOSITION (GRAVEL, SAND, SILT, CLAY, ORGANICS)
CONTAMINATION/CULTURE
DEPTH
DRAINAGE SAMPLE SITE
E/W
ELEVATION
FIELD ROCK NAME
FLOW RATE
GRAIN SIZE
GRID LINE
GRID STATION
MAGNITUDE
N/S
OVERBURDEN CLASSIFICATION
OVERBURDEN FEATURES
OVERBURDEN STRUCTURES
pH
PRECIPITATE/STAIN
SAMPLE IDENTIFIER
SAMPLE TYPE
SLOPE (MAGNITUDE, DIRECTION)
SOIL CLASSIFICATION
SOIL HORIZON
STATUS
THICKNESS
TOP OF INTERVAL
UTM COORDINATES (ZONE, EASTING, NORTHING)
WIDTH

Figure 18. Dictionary/Glossary "Keyword" List

COLOUR (2 character, alphabetic): Up to 2 colours can be recorded.

WT	White
BF	Buff (Beige)
BR	Brown
BK	Black
GY	Grey
GN	Green
OG	Orange
YL	Yellow
RD	Red
RS	Rust
PR	Purple
PK	Pink
BU	Blue
OV	Olive

COMPOSITION (4 digit, numeric): Bulk mechanical composition of the actual material sampled in terms of its Sand (2.000 to 0.0625 mm), Silt (0.0625 to 0.004 mm), Clay (< 0.004 mm) and Organic content. Record relative amounts using

0 = 0
1 ≤ 10
2 > 10 ≤ 20
3 > 20 ≤ 30
4 > 30 ≤ 40
5 > 40 ≤ 50
6 > 50 ≤ 60
7 > 60 ≤ 70
8 > 70 ≤ 80
9 > 80 ≤ 90
X > 90

GRAIN SIZE (2 character, alphabetic): From 1 to 3 grain sizes can be recorded from the maximum component (right justified) decreasing to the minimum (left justified):

CY	Clay		< 0.004
SL	Silt	> 0.004	≤ 0.0625
TS	Total sand	> 0.0625	≤ 2.000
FS	Fine sand	> 0.0625	≤ 0.250
MS	Medium sand	> 0.250	≤ 0.500
CS	Coarse sand	> 0.500	≤ 2.000
GV	Gravel	> 2.000	≤ 256.000
GN	Granules	> 2.000	≤ 4.000
PB	Pebbles	> 4.000	≤ 64.000
CB	Cobbles	> 64.000	≤ 256.000
BL	Boulders	> 256.000	

Figure 19. "Keyword" Dictionary/Glossary definitions for COLOUR, COMPOSITION and GRAIN SIZE

OVERBURDEN CLASSIFICATION (2 character, alphabetic): The genetic classification for type of overburden material sampled:

Al - Alluvium - reworked by fluvial processes (sands & gravels), includes outwash and present day fluvial deposits
CL - Colluvium - mass movement, slump, talus, creep
FL - Fluviolacustrine deposits
GF - Glaciofluvial deposits
LK - Lacustrine deposits
MR - Marine deposits
0D - Organic debris
SG - Sands and gravels, derivation unknown
TU - Till, typed undefined
TL - Lodgment till
TM - Melt-out till
TF - Flow till
TW - Water laid till
TD - Deformation till
TA - Ablation till
UC - Unclassified

SOIL HORIZON (2 character, alphabetic): The specific soil horizon sampled:

LH - Leaf layer, undecomposed vegetation lying on the ground surface
AH - Dark black, decomposed organic horizon, usually no deeper than 15 cm from the surface
AE - Grey to white (occasionally brown) leached mineral horizon near ground surface, usually sandy; accompanied by BF or BT horizon at depth
BH - Black, organic-rich mineral horizon at depths greater than 15 cm
BF - Red brown, iron-rich horizon (Podzol)
BT - Brown, clay-rich horizon (Luvisol)
BG - Horizon which is water-saturated most of the year, identified by red brown mottles (Gleysol)
BM - Brown horizon which is only slightly different in appearance from underlying parent material C_1, C_2,
C_3, etc. - Parent material for soil
CA - White calcium carbonate precipitate in C horizon
0_1, 0_2, 0_3, etc. - Bog samples at various depths
TF - Talus fines

Figure 20. "Keyword" Dictionary/Glossary definitions for OVERBURDEN CLASSIFICATION and SOIL HORIZON

Properly planned, carried out and documented sample collection and field data acquisition are the keys to the success of any geochemical exploration program.

SAMPLE ANALYSES

After a sample has been collected, it must be prepared (dried, sieved, ground, etc.), decomposed and later analyzed ([redacted]). An understanding of the correct preparation procedures, the various methods of sample decomposition (digestion, fusion), the capabilities and limitations of the important analytical methods and the correct chemical analysis for a particular situation are critical to optimizing the potential of exploration geochemistry. The analytical procedure chosen must be sensitive enough to detect elements present in very small (i.e. background) concentrations; it must be reliable enough (accurate and precise) that chances of missing an important anomaly are minimized; and, it must be both rapid and economically feasible, which is dependent to a degree on the number of samples to be processed.

The mode of occurrence of trace elements in natural materials and the techniques of sample preparation, decomposition, separation and estimation will be briefly reviewed. But before discussion starts on these items, I must stress the critical need for us to control the quality

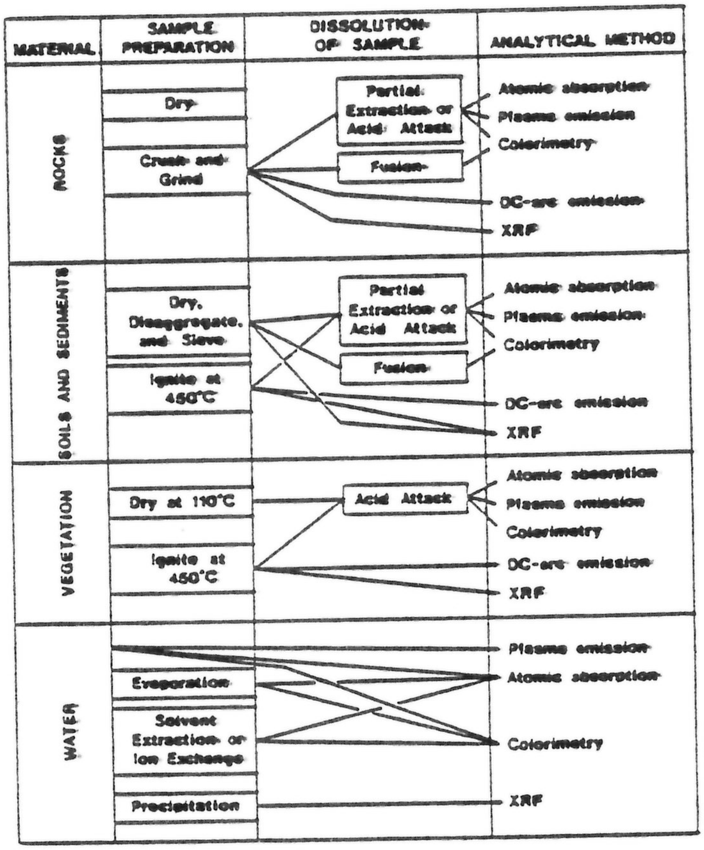


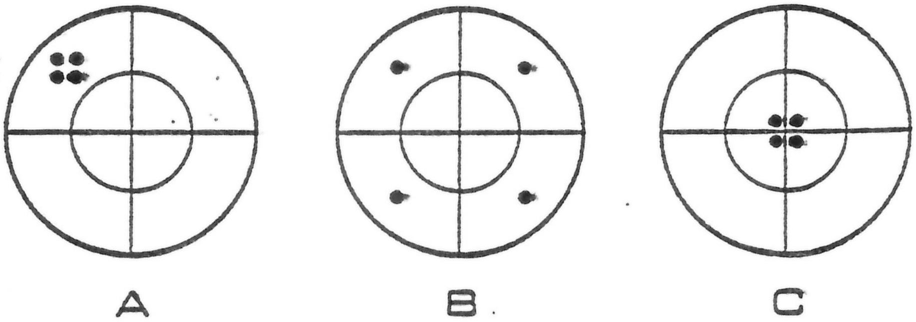
Figure 21. Some of the pathways for preparation, dissolution and analysis of exploration samples

of the analyses we are obtaining from commercial laboratories:

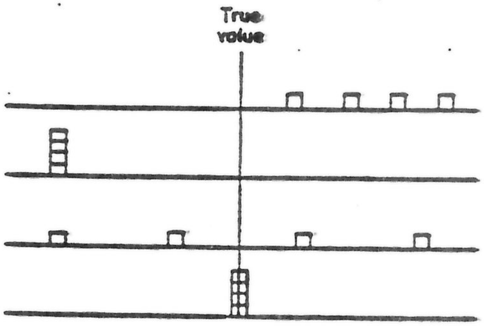
A) Quality Control

Problems in our geochemical programs could arise, indeed probably have arisen and gone undetected, due to lack of *quality control* on analytical data. Large sums of money could be and probably have been spent following-up geochemical anomalies which have never been verified or evaluated for analytical credibility. Quality control is also essential to assess the relationship of analytical data obtained over a number of years either from one laboratory or from a number of laboratories using the same, modified or entirely different analytical techniques. Reliable analyses are required if significant anomalies and patterns are to be detected with any degree of confidence. The reliability of the analyses must be evaluated in terms of both precision and accuracy ([redacted]. [redacted] is a measure of the reproducibility of the analytical determinations. [redacted] is a measure of how close the determined value is to the true (preferred) value.

The precision of the analyses can be determined by multiple analyses of a single sample or, *preferably*, by duplicate analyses of many samples from the area being surveyed. Systematic duplicate analyses ([redacted]) are relatively effective for estimating the precision of the reported analyses and, in addition, can serve to detect the



Precision	Good	Poor	Good
Accuracy	Poor	Good	Good



Precision	Accuracy
Poor	Poor
Good	Poor
Poor	Good
Good	Good

Figure 22. Precision and Accuracy

SAMPLE IDENTIFIER	SAMPLE STATUS	
DA00001	81	(BD)---Blind duplicate split of DA00018
02	00	
03	00	
04	00	
05	00	
06	00	
07	00	
08	9G	(RC)---Reference Control "G"
09	00	
10	00	
11	00	
12	00	
13	10	(FD1) Field duplicate array
14	11	
15	20	(FD2)
16	21	
17	00	
18	00	
19	00	
DA00020	00	

Figure 23. Model for insertion of control samples to determine analytical accuracy and precision

occasional large errors caused by mistakes in procedure, misnumbering or other blunders. Analytical error also commonly varies with element concentration, so multiple analyses of a single sample does not allow an estimate of precision over a range of concentrations. Replicate determinations on several samples of differing concentration are therefore desirable. The working range of an analytical technique is the concentration range over which the relationship between metal content and machine response is linear. This range is bound at the top and bottom by the upper and lower detection or sensitivity limits of the method as depicted in [redacted] by plotting duplicate results. A graphical presentation of duplicate results is an adequate, effective and expedient way of determining analytical precision as illustrated in [redacted] Remember, precision is an estimate, and no absolute connotation should be assigned to a given precision value (i.e. a graphically estimated precision of ±12.5% could well be ± 10% or ± 15%, in fact rounding off to 5, 10, 15...30, 35, etc. is recommended). While graphical methods for determining precisions are recommended, there are also a number of mathematical formulas used for calculating precision:

i) For analyses on each duplicate pair of data ([redacted]:

$$\left(\frac{V_1 - V_2}{\bar{x}_{V_1 V_2}}\right) \times 100 = \pm \text{ \% Precision}$$

V_1 = value of element in first member of a pair
V_2 = value of element in second member of a pair
$\bar{x}_{V_1 V_2}$ = arithmetic mean value of element for V_1 and V_2

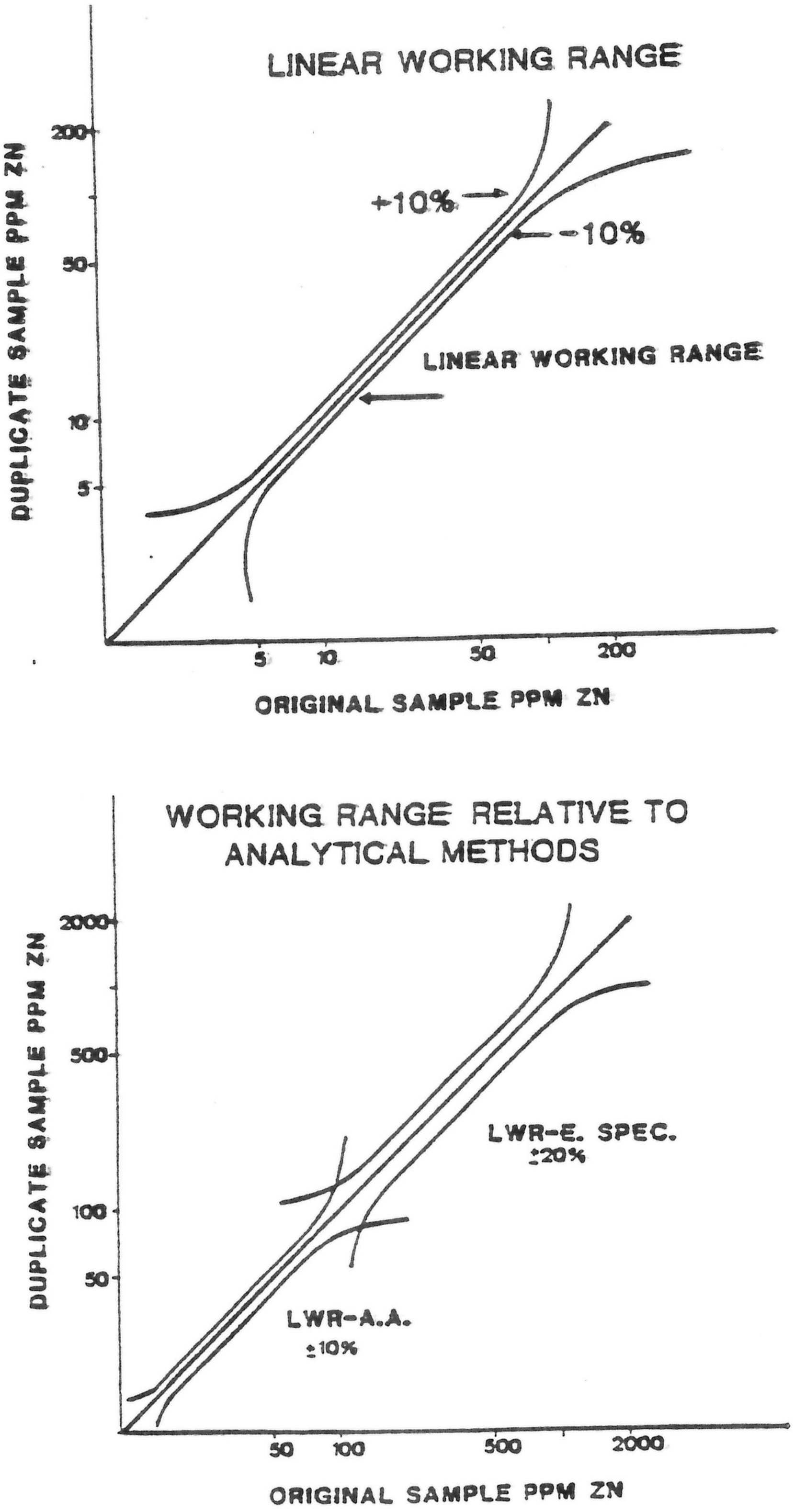


Figure 24. Linear working range

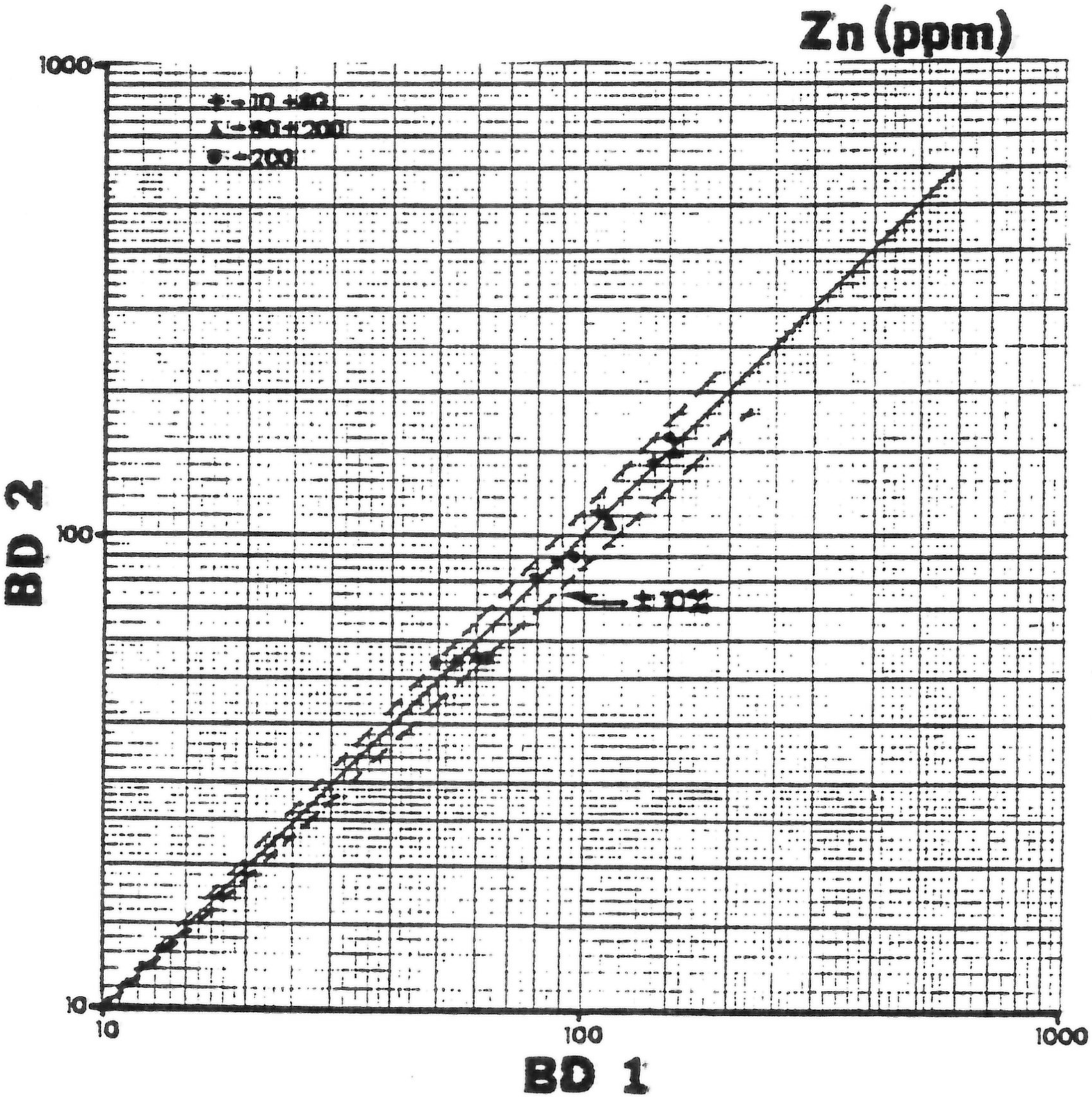


Figure 25. Precision limits for Zn determined graphically using blind duplicate sample pair data: Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

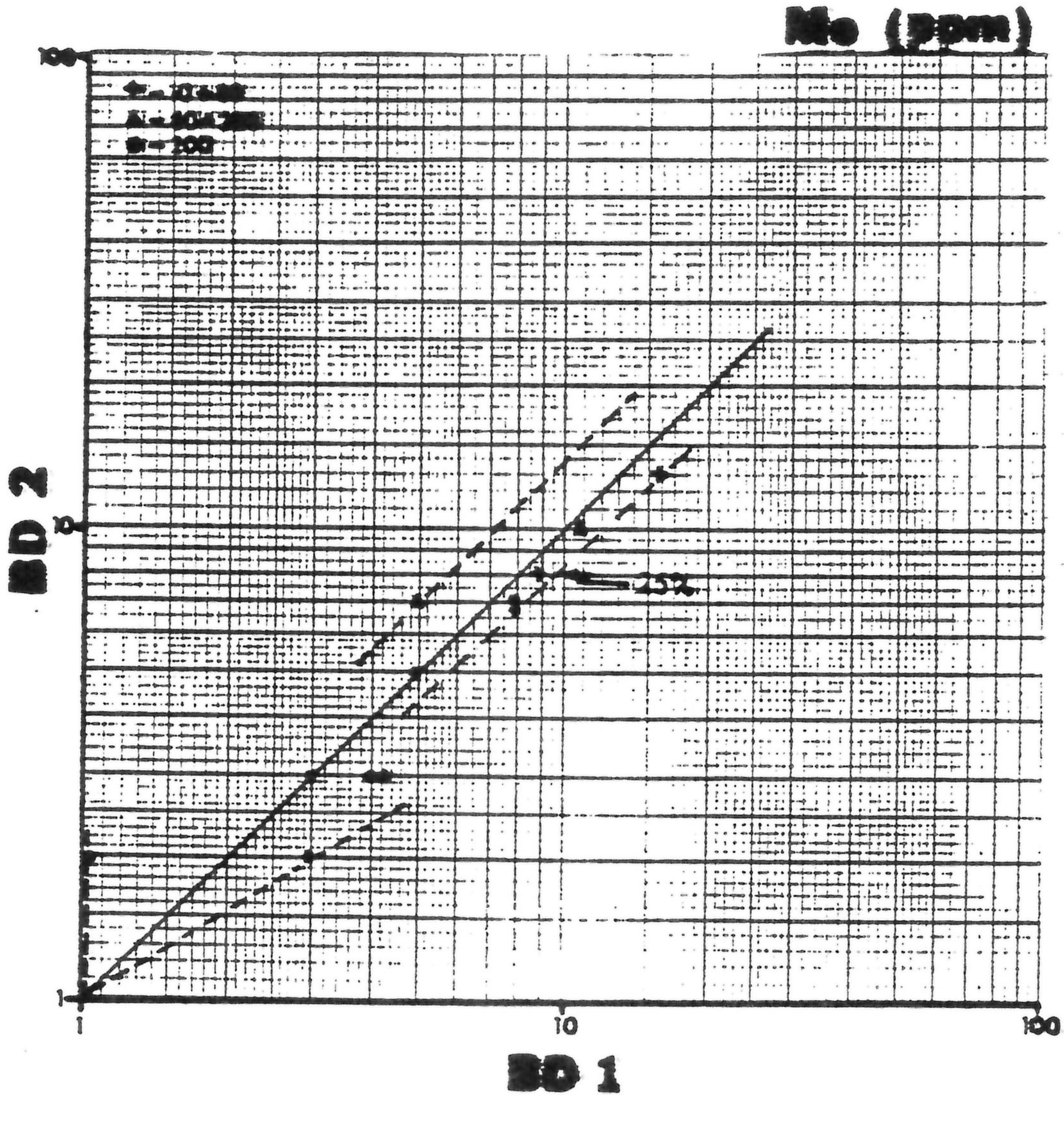


Figure 26. Precision limits for Mo determined graphically using blind duplicate sample pair data: Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

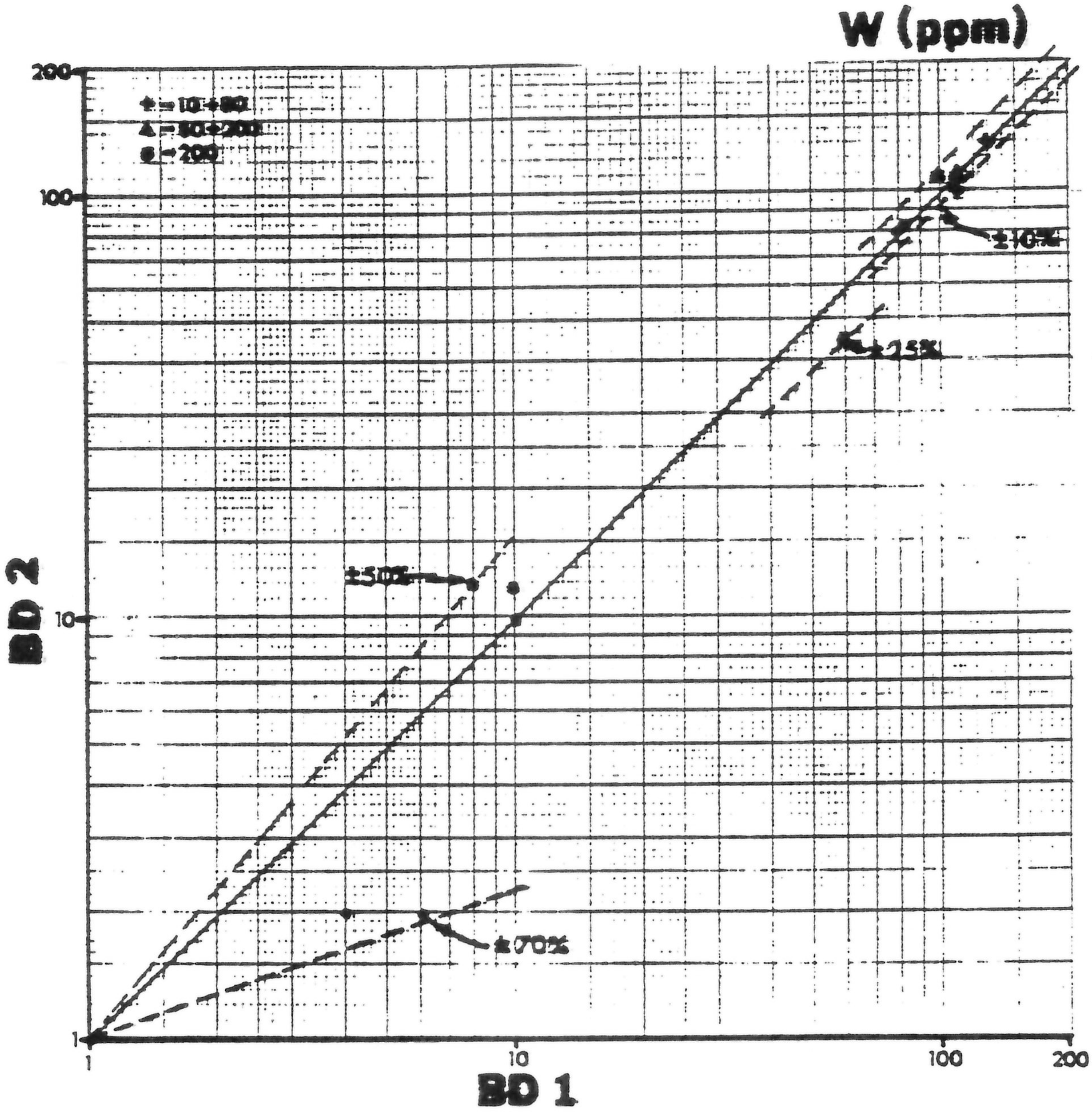


Figure 27. Precision limits for W determined graphically using blind duplicate sample pair data: Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

Sample Numbers	Mesh Size	Cu (ppm)	±P (%)	Pb (ppm)	±P (%)	Zn (ppm)	±P (%)	Ni (ppm)	±P (%)	Ag (ppm)	±P (%)	Mo (ppm)	±P (%)	Fe (ppm)	±P (%)	As (ppm)	±P (%)	F (ppm)	±P (%)	W (ppm)	±P (%)	Sn (ppm)	±P (%)
MC82019001/004	-10+80	85/85	0	46/47	2	110/11	2	16/17	6	0.8/0.8	0	16/13	21	3.7/3.	3	90/84	7	440/420	5	110/10	10	26/2	4
	-80+20	95/95	2	45/45	0	115/10	7	15/15	0	1.0/1.0	0	11/10	10	4.3/4.	0	80/77	4	420/390	7	100/11	10	15/1	18
	-200	83/84	1	49/46	6	90/90	0	10/12	18	1.3/1.3	0	8/7	13	4.4/4.	0	87/83	5	340/320	6	80/80	0	17/1	19
MC82019021/025	-200	14/11	24	23/24	2	64/56	13	14/14	0	1.0/0.2	13	3/3	0	4.5/4.	12	32/33	3	210/200	5	8/12	40	4/4	0
MC82267001/004	-200	34/33	3	21/16	27	62/56	10	22/22	0	0.5/0.6	18	4/3	28	2.7/2.	0	16/18	11	330/235	33	10/10	0	9/13	36
MC82267021/026	-200	69/65	6	37/36	3	97/93	4	24/25	7	*<0.1/<0.	0	8/7	13	2.3/2.	0	36/34	40	485/520	7	60/45	28	15/9	50
MC82267041/044	-200	61/65	6	28/27	4	80/83	7	35/35	0	0.1/0.1	0	3/2	40	2.9/2.	0	78/78	0	470/430	9	10/12	18	8/6	29
MC82267061/064	-200	20/19	5	14/12	15	55/55	0	26/26	0	<0.1/ 0.	0	* 1/2	67	2.0/2.	0	11/13	16	540/470	14	4/2 *	67	12/1	67
MC82267081/085	-200	25/22	13	16/18	12	50/55	10	20/21	5	0.2/0.1	67	4/3	28	2.2/2.	4	31/30	3	475/390	20	6/2	100	4/10	86
MC82267101/106	-10+80	154/172	11	32/33	3	146/14	1	88/88	0	0.3/0.4	29	9/8	12	3.1/3.	0	42/51	19	820/860	5	130/13	0	12/1	18
	-80+20	163/185	13	22/27	20	154/15	1	98/101	3	0.3/0.4	29	5/7	33	3.2/3.	3	42/45	7	930/800	6	110/11	0	12/9	28
	-200	157/177	12	15/19	24	152/16	6	105/10	1	0.2/0.1	67	5/5	0	3.2/3.	0	38/34	11	1100/122	11	80/80	0	9/14	38
Number of blind duplicate pairs		12		12		12		12		12		12		12		12		12		12		12	
Mean precision $\left(\frac{\Sigma P_{1-n}}{n}\right) = P_{\bar{x}}$		±8%		±10%		±5%		±3%		±29%		±22%		±2%		±10%		±11%		±12%		±33%	

Precision = $\left(\frac{BD_1 - BD_2}{\bar{x}_{BD_1 BD_2}}\right)$ X 100 = ±P(%)

* Lower detection limit

Table 7. Precision limits calculated from blind duplicate pair data: Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

ii) Multiple analyses on a single sample ([redacted]):

$\frac{2s}{\bar{x}} \times 100 = \pm$ % Precision at the 95% confidence level

s = arithmetic standard deviation
$\bar{x}$ = arithmetic mean

Precision levels worse than ±50% are indicative of data at or below the realistic detection limit for the analytical method used. Such data lie outside the linear working range.

Ideally, in order to evaluate the accuracy of a geochemical analysis, the true content of an element (estimated by at least 25 determinations) in some sample must be known and compared with determinations by the analytical method in question. The simplest type of inaccuracy is a constant deviation (always high or always low) or constant percentage deviation (plus 20% of true value or minus 10% of true value). In more complicated cases, the error depends on the form of the element or on the concentration of some other interfering element. The simplest method for estimating accuracy is analysis of one or more reference control samples whose chemical composition has been carefully documented by numerous analyses ($n > 25$) at one or a number of laboratories. An example of a graphical method for portraying accuracy is illustrated in [redacted] Accuracy can also be determined mathematically with the calculated accuracy for a given reference control sample being considered acceptable only if it falls within the $\bar{x} \pm 2.5s$ (i.e. arithmetic mean ($\bar{x}$) and standard

Sample number	Cu	Pb	Zn	Mo	Ni	Ag	Fe	As	F	W	Sn	Bi
	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
WC82019009	92	29	110	3	43	<0.1*	3.6	35	760	<2*	6	
WC82019024	82	31	122	<1	39	0.1	3.6	38	700	4	5	
WC82267092	80	24	106	1	39	0.1	3.1	36	690	4	9	
WC82267117	82	27	108	3	40	<0.1	3.3	39	810	8	9	
Number of samples (n)	4	4	4	4	4	4	4	4	4	4	4	
Range (min-max)	80-92	24-31	106-122	<1-3	39-43	<0.1-0.1	3.1-3.6	35-39	690-810	<2-8	5-9	
Arithmetic mean ($\bar{x}$)	84	28	112	2	40	--	3.4	37	740	4	7	
Standard deviation (s)	5	3	7	1.3	2	--	0.2	2	56	3	3	
Coefficient of variation (c.v.) $\left(\text{c.v.} = \frac{s \times 100}{\bar{x}}\right)$	6%	11%	6%	66%	5%	--	7%	5%	8%	72%	42%	

* Lower limit of analytical detection

Table 8. Precision limits (i.e. 2x c.v.) calculated using multiple analyses of a single sample (Reference Control Trench 5): Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

Sample number	Cu ppm	Pb ppm	Zn ppm	Mo ppm	Ni ppm	Ag ppm	Fe %	As ppm	F ppm	W ppm	Sn ppm	Bi ppm
WC82267014	241	35	85	6	19	<0.1*	2.6	43	505	80	18	
WC82267035	239	32	88	7	20	<0.1	2.6	45	640	85	15	
WC82267058	249	36	89	8	21	<0.1	2.5	44	710	45	17	
WC82267070	233	34	90	8	21	0.1	2.6	51	690	60	11	
WC82019030	207	34	95	8	16	<0.1	2.7	47	530	60	13	
Number of samples (n)	5	5	5	5	5	5	5	5	5	5	5	
Range (min-max)	207-249	32-36	85-95	6-8	16-21	<0.1-0.1	1.7-2.6	43-51	505-710	45-85	11-18	
Arithmetic mean ($\bar{x}$)	233	34	89	7	19	--	2.6	46	615	66	15	
Standard deviation (s)	16	1.5	3.6	0.9	2	--	0.1	3	93	16	3	
Coefficient of variation (c.v.) $\left(\text{c.v.} = \left(\frac{s}{\bar{x}} \times 100\right)\right)$	7%	4%	4%	12%	11%	--	3%	7%	15%	25%	19%	

* Lower limit of analytical detection

Table 9. Precision limits (i.e. 2x c.v.) calculated using multiple analyses of a single sample (Reference Control Trench 9): Surficial Geology and Overburden Geochemistry Orientation Study, Sisson Brook-Napadogan Brook, N.B.

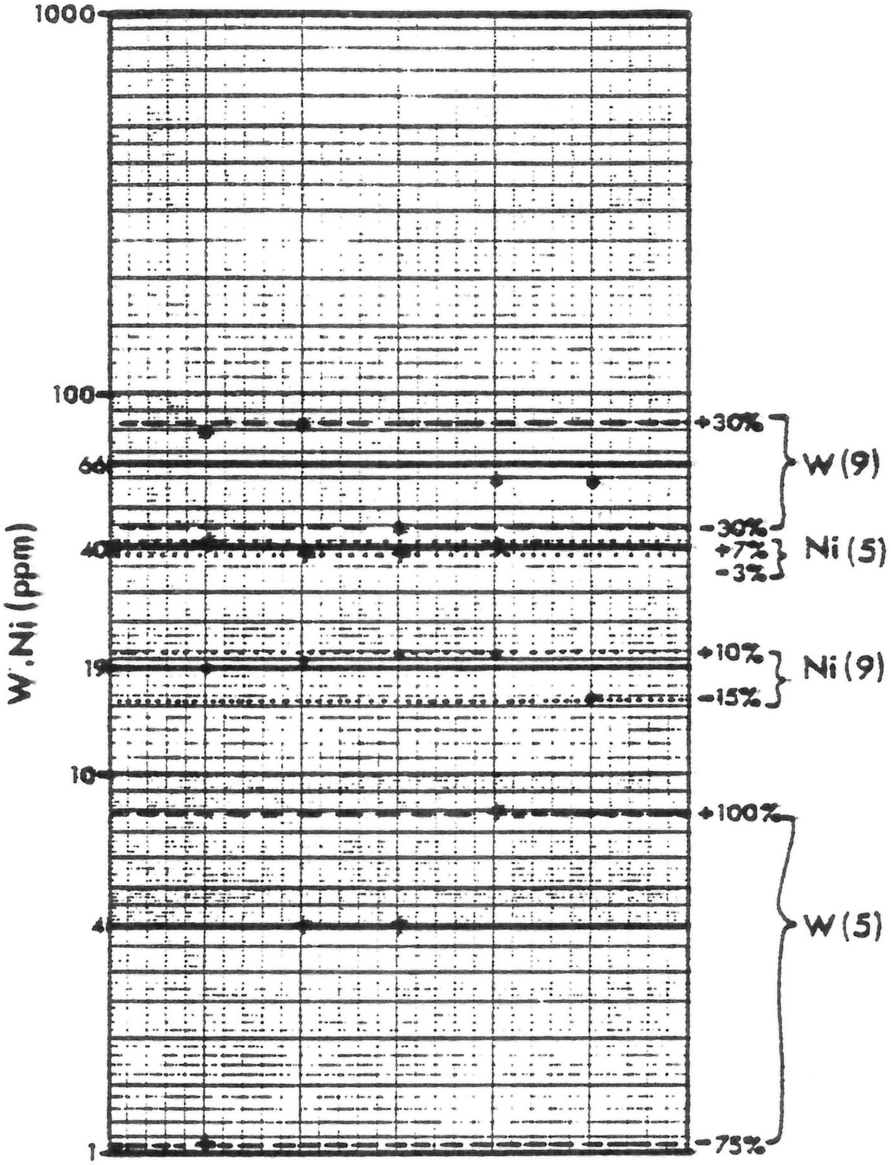


Figure 28. Graphical evaluation of analytical accuracy for W and Ni for reference control samples from Trenches 5 and 9, Sisson Brook, N.B.

deviation (s)) limits as determined by at least 25 previous analyses ([redacted]).

> Rejection or acceptance of data for each element in a given block of 20 samples ([redacted]) is decided by the estimated precision and accuracy values. Data failing to meet the established specification for any given element are rejected, and all 20 samples must be reanalyzed for that element.

There is a critical need for us to prepare or obtain a number of reference control standards and document their elemental concentrations in order to allow evaluation of the quality of all future analytical data.

Another type of variation that should be periodically assessed, although not necessarily as often as analytical precision and accuracy, is the elemental variation at the sample site. As illustrated on [redacted] (i.e. field duplicate array), two identical samples are collected at a given site (i.e. 10 and 20) and, after preparation, split in two (i.e. 10 and 11, 20 and 21) for analyses. If only the original pair (i.e. 10 and 20) were collected and analyzed, any elemental variation detected could not be reliably accredited to sample site variation or to analytical variation. Splitting each sample into two parts for analyses allows confident assessment of both the analytical and sample site component of any variation. This test need not be routinely carried out, but it should be inserted on occasion to allow an assessment of elemental variablility between sample sites relative to that at an individual site. Via this method, the significance of any elemental variation within a given sampled area can be realistically assessed.

The actual procedure for including a blind duplicate, reference control and field duplicate array of control samples into the sampling design is illustrated in Figure 23. Normally, in each block of 20 samples, there are 18 routine samples, one blind duplicate sample and one reference control sample. The blind duplicate is a split of one of the 18 field samples, and the reference control sample is a portion taken from one of the bulk reference samples available. Insertion of control samples requires that some forethought be put into the sampling design. Prenumbering the sample bags and taping shut and coding the masking tape (i.e. BD = blind duplicate, RC = reference control) to identify the control samples ensures error-free sampling and that empty bags will be left within the sample sequence for insertion of the control samples. If a field duplicate array is to be used in a block of 20 samples, there will only be 16 routine samples, one blind duplicate sample, one reference control sample and two field duplicate samples (splits of two of the routine samples identified as FD1 and FD2 on the tape shutting their bags).

The procedure for the preparation and insertion of the blind duplicate, reference control and field duplicate array of control samples, before analyses occur at the laboratory, is not simple. In order to insure security in our evaluation of data credibility, the control samples have to be secretly inserted after preparation of all samples.

If the preparation is done in the field (i.e. sieving soils, overburden or stream sediments), the control samples can easily be secretly inserted before being sent to a commercial laboratory for analyses.

However, in most instances, all or at least the final crushing and grinding stages of sample preparation are done at the commercial laboratory doing the analyses. In this case, there are a number of choices, each with shortcomings, for insertion of the control samples. Sample numbers used in the examples described are from Figure 23:

i) Field preparation of the control samples can generally only be carried out on unconsolidated sample materials (i.e. soils, overburden, stream sediments, etc.). After drying, sieve the blind duplicate sample (i.e. DA00018) to the desired mesh size, say -80 mesh. Place one-half of the oversized material (+80 mesh) in each blind duplicate members bag (i.e. DA00001 and DA00018). Extra clean oversized material may be added to make up the volume if desired, but use caution! After carefully mixing the -80 mesh material, to assure homogeneity, add one-half to the bag of each blind duplicate member as with the oversize. Field duplicate pairs (i.e. DA00013 and DA00014 and DA00015 and DA00016) can be treated in exactly the same fashion. To insert a reference control sample (i.e. DA00008), simply place some dried clean oversized material (+80 mesh) in the reference control bag and add some of the bulk reference control material (i.e. reference control "G") to the same bag. Most reference control materials are generally prepared to -200 mesh, but be sure to verify this. When the blind duplicate pair of samples, field duplicate array of samples and the reference control samples are sieved to -80 mesh in the laboratory, only the desired material previously field-prepared or inserted will pass through the -80 mesh sieve and be used for the analyses.

ii) If the preparation of the samples is done at the laboratory, then a person has to be appointed to go to the laboratory after the samples have been prepared to divide the blind duplicate and field duplicate samples into two equal homogeneous parts and to place each half in the appropriate vials/envelopes. The reference control sample can also be added to the appropriate vial/envelope.

iii) We might have one laboratory prepare the samples and return them to us where the control materials can be inserted before sending them back to that or another laboratory for analyses.

There is no ideal or simple way of inserting the control samples, each geologist or geochemist will have to use the technique best suited to their situation.

B) Mode of Occurrence of Trace Elements

The form in which trace elements occur in soil, stream sediment, rock or any other material determines their chemical behaviour and how they respond within the natural environment or to laboratory procedures. Four major types of occurrence are ([redacted]):

i) Major element in trace mineral (Pb in galena, Cu in malachite)

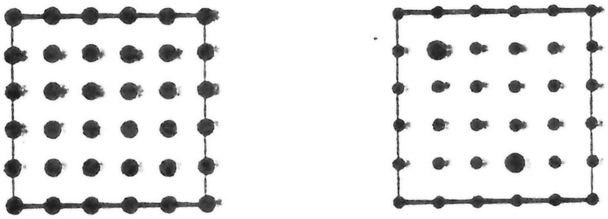
ii) Trace element in crystal structure of a well-crystallized mineral (Zn in magnetite, Pb in K-feldspar or Cu in biotite)

iii) Trace element in poorly-crystallized phase or adsorbed on such material and trapped by further precipitation

iv) Trace element adsorbed on the surface of a colloidal particle of Fe-Mn oxide, clay or organic material, or in the exchange layer of a clay mineral.

It is clear that a trace element enclosed by a host mineral which is inert in either the natural or laboratory environment will remain in the solid phase and can only be affected by physical processes, such as sorting by size or density of the particle. In contrast, a trace element occurring as a trace mineral or as an adsorbed ion may be taken directly into solution by appropriate changes in the surrounding solution. Trace elements in the lattice of major minerals can go into solution only after decomposition of the host.

The minerals formed during weathering are generally fine grained, poorly crystalline and have a large surface area. As a result, they may be dissolved or modified by relatively mild chemical treatments. The silicates and



Trace mineral

Trace element in well-crystallized mineral

Trace element in fine-grained poorly crystallized mineral

Trace element adsorbed on surface

Figure 29. Schematic diagrams of four major modes of occurrence of trace elements (●)

oxides of igneous and metamorphic rocks (and their detrital grains in sedimentary rocks, soils and stream and glacial sediment) generally require more drastic chemical treatment for decomposition. Trace minerals have a wide range of properties, ranging from phases soluble in water to zircon and other heavy resistant minerals.

The stability of Fe and Mn-oxides is a function of acidity (pH) and oxidation potential (Eh) [redacted]. Oxides of both Fe and Mn are dissolved by either acid or reducing solutions. The Mn-oxides are more easily dissolved than the Fe-oxides. By an appropriate choice of acids or reducing agents, Fe or Mn-oxides or both may be selectively dissolved from samples of soil or stream sediment, leaving the more resistant minerals behind. Conversely, if the chemical conditions are kept within or near the field of stability of the Fe and Mn-oxides, trace metals enclosed in them should be unaffected. Similarly, organic materials and sulphides are stable only under reducing conditions and may therefore be dissolved by strongly oxidizing treatments. Clays, micas, feldspars and mafic silicates are only slowly decomposed by weak acids or bases because silica and alumina are relatively insoluble in such solutions [redacted]. Many of these silicates are only slowly decomposed even in hot concentrated acids and therefore are relatively unaffected by conditions that dissolve Fe or Mn-oxides.

The form in which trace elements occur in waters in streams, lakes, groundwaters and so on also determines their

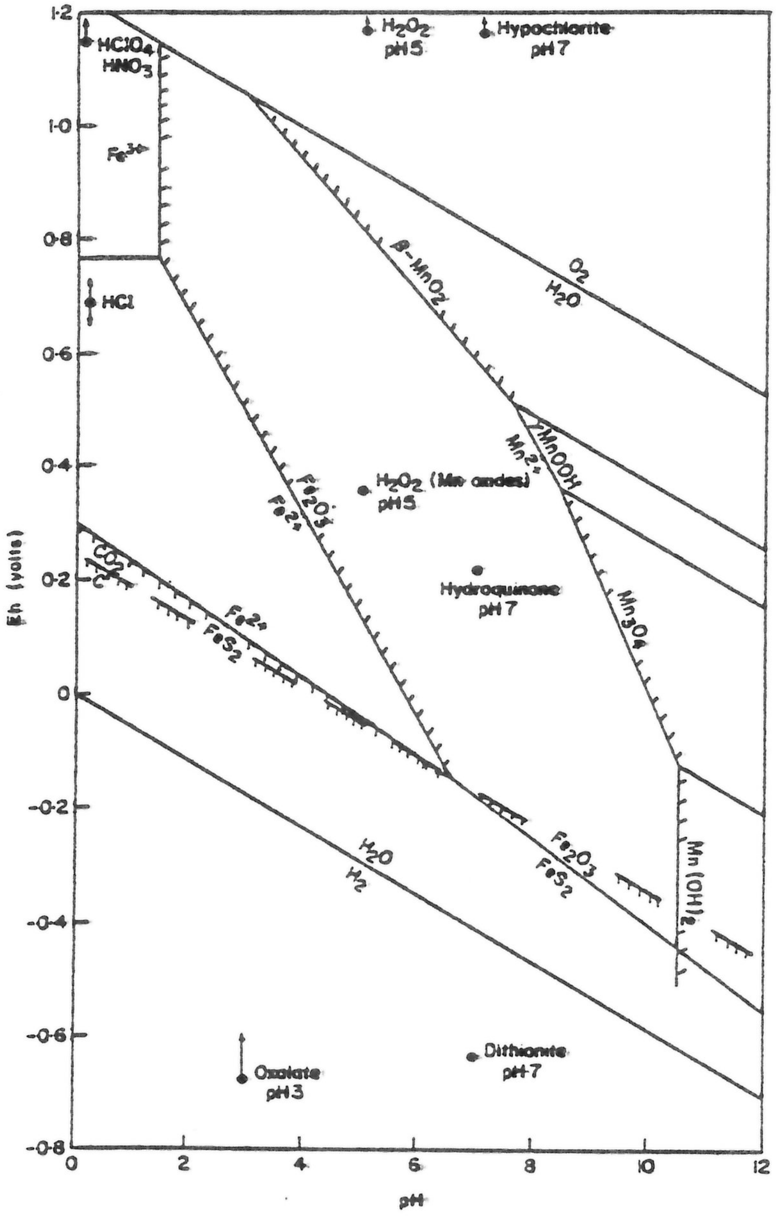


Figure 30. Stability of Fe-oxide, Mn-oxide, pyrite and organic matter (C) as a function of Eh and pH, as compared to conditions imposed by several types of selective leach solutions. Solid phases are stable on hatched sides of boundaries.

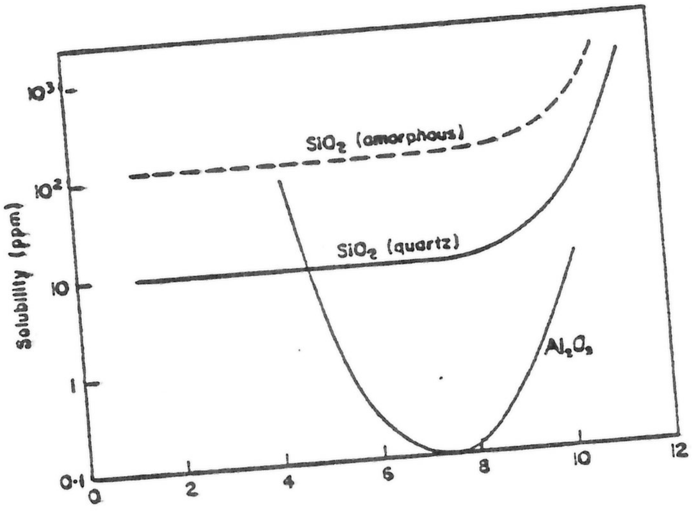


Figure 31. Solubility of aluminosilicates vs pH, as indicated by solubility of Al and Si

chemical behaviours in response either to the natural environment or to laboratory procedures. If an element is to move with the water, it must occur either in soluble form or as a component of a stable suspension. Knowledge of the form is also important in deciding how to collect, treat and analyze the water. The following are the most important mobile phases:

i) Cations or cationic complexes (+)
   (Zn^{2+}, Cu^{2+}, UO_2^{2+}, $CaOH^+$)
ii) Anions or anionic complexes (-)
   (SO_4^{2-}, MoO_4^{2-}, $UO_2(CO_3)_3^{4-}$)
iii) Unchanged atoms, molecules or ion pairs
   (Rn, He, O_2, $H_4SiO_4^0$, $PbCO_3^0$)
iv) Organic complexes
v) Suspended colloidal particles
   (colloidal Fe, Al & Mn oxides & hydroxides)
vi) Ions adsorbed on suspended matter.

In collecting, treating and analyzing water samples, care must be taken to identify the form of the desired element, to retain it in the sample and, if possible, to exclude complicating effects of other forms. Precipitation from solution, collection on ion-exchange resins or extraction into an immiscible phase may extract only the ionic forms. Filtration through membrane filters and similar devices can remove the coarser suspended material, but, in practice, particles less than 0.1 um are difficult to separate. Acidification may dissolve particles and change the form of others. Oxidation by ashing the evaporated residue or by treatment with an oxidizing acid may be required to liberate metal strongly bound by organic matter.

Ground water usually carries most of its load of metal in one of the ionic forms, with lesser proportions traveling as stabilized colloidals, sols and organic complexes.

Surface water, on the other hand, because of the effect of both sunlight and increased aeration and turbulence, carries a large, variable and unpredictable fraction of its metal content in non-ionic form, principally as constituents of soluble organic matter and both inorganic and organic suspensoids.

C) Sample Preparation

There are many variables which enter into the preparation of a geochemical sample for analysis, not the least of which is the nature of the sample itself. Water samples can generally be analyzed directly or may require filtering and/or preconcentration. However, most geochemical samples are soils, sediments, rocks or vegetation which require some preparation.

The main processes to be considered in preparing a sample for chemical analyses are drying, crushing, sieving, subsampling, (coning and quartering) and grinding. No matter how carefully a sample may have been collected in the field, the data obtained from it will be worthless if it is not prepared correctly. One must constantly keep in mind that the small amount of sample which is actually analyzed, anything from 0.1 gram to perhaps 100 grams, represents an extremely small part of any area with mineral potential or an ore body. Most analysts try to use a representative 1 to 5 gram sample for digestion or fusion. Larger weights up to 35 grams are used for assays. Reproducibility and accuracy on a sample of 0.1 gram is likely to be low, and 100 gram samples are generally too cumbersome for most geochemical analyses.

i) Drying: Drying is necessary before samples can be properly sieved. Samples collected in paper envelopes can be hung in camp to dry, either in ovens or using plastic sheeting and the sun or just the sun itself. Wet bags decay. Samples to be analyzed for readily extractable metals or similar components should not be completely dried because the form the element occurs in may change. Samples intended for the analysis of Hg and other volatile elements must not be dried at elevated temperatures in ovens.

ii) Crushing and Grinding: Crushing and grinding may be necessary to reduce the size of lumps in the case of stream sediments and soils and are needed to reduce rock samples so they will pass through an appropriate screen. In the case of rock samples, in order to obtain a truly homogeneous and representative sample, they should be pulverized to pass through not less than a 100 mesh screen and preferably a 200 mesh screen. Ceramic plate crushers, ball mills or disc mills are commonly used to avoid contamination from ferroalloy or tungsten-carbide crushers or mills ([redacted]).

iii) Sieving: Sediment and soil samples, after crushing (if necessary), are generally passed through an 80 mesh screen unless an orientation survey indicates another fraction is preferable. The screen should be made of nylon or aluminum to prevent contamination from brass or stainless steel. This sieving has two purposes: (i) rejection of coarse fragments of quartz, organic litter, and other materials relatively poor in trace metals and (ii) production of a fine grained homogeneous product from which representative subsamples may be conveniently taken. Sizes of sieves should be specified by the dimension of the sieve opening because sieves of the same nominal mesh may differ in the size of their openings ([redacted]).

Mineral separations of various other kinds may be made on clastic samples prior to chemical analysis. These separations take advantage of the principal physical properties of the minerals, particularly the density, magnetic susceptibility or electrical properties. The preparation of panned concentrates and heavy mineral concentrates [redacted] are examples of such separation procedures in use by Kidd.

iii) Subsampling: When small portions of pulverized rock, soil or sediment are removed from a larger volume for further processing or analysis, care must be taken that these sub-samples are representative. There is a

Material	Potential contaminants
Grinding equipment	
Steel and iron grinding plates	Fe, Co, Cr, Cu, Mo, Mn, Ni, V
Alumina ceramic plates	Al, Cu, Fe, Ga, Li, Ti, B, Ba, Co, Mn, Zn, Zr
Tungsten carbide	Co, Ti, W
Lubricants	Mo
Packaging materials	
Polythene	Ti, Ba, Zn, Cd
Polypropylene	Ti
PVC	Ti, Zn, Na, Cd
Brown paper	Si
Rubber	Zn

Figure 32. Potential contaminants from laboratory materials

Approximate aperture (μm)	B.S.	ASTM	Tyler
2000	8	10	9
1000	16	18	16
850	18	20	20
420	36	40	35
355	44	45	42
300	52	50	48
250	60	60	60
212	72	70	65
180	85	80	80
150	100	100	100
125	120	120	115
90	170	170	170
75	200	200	200
63	240	230	250
53	300	270	270
45	350	325	325
38	--	400	400

Table 10. Approximate equivalent mesh sizes in the British Standard (B.S.), American Society Testing Material (ASTM) and Tyler sieve series

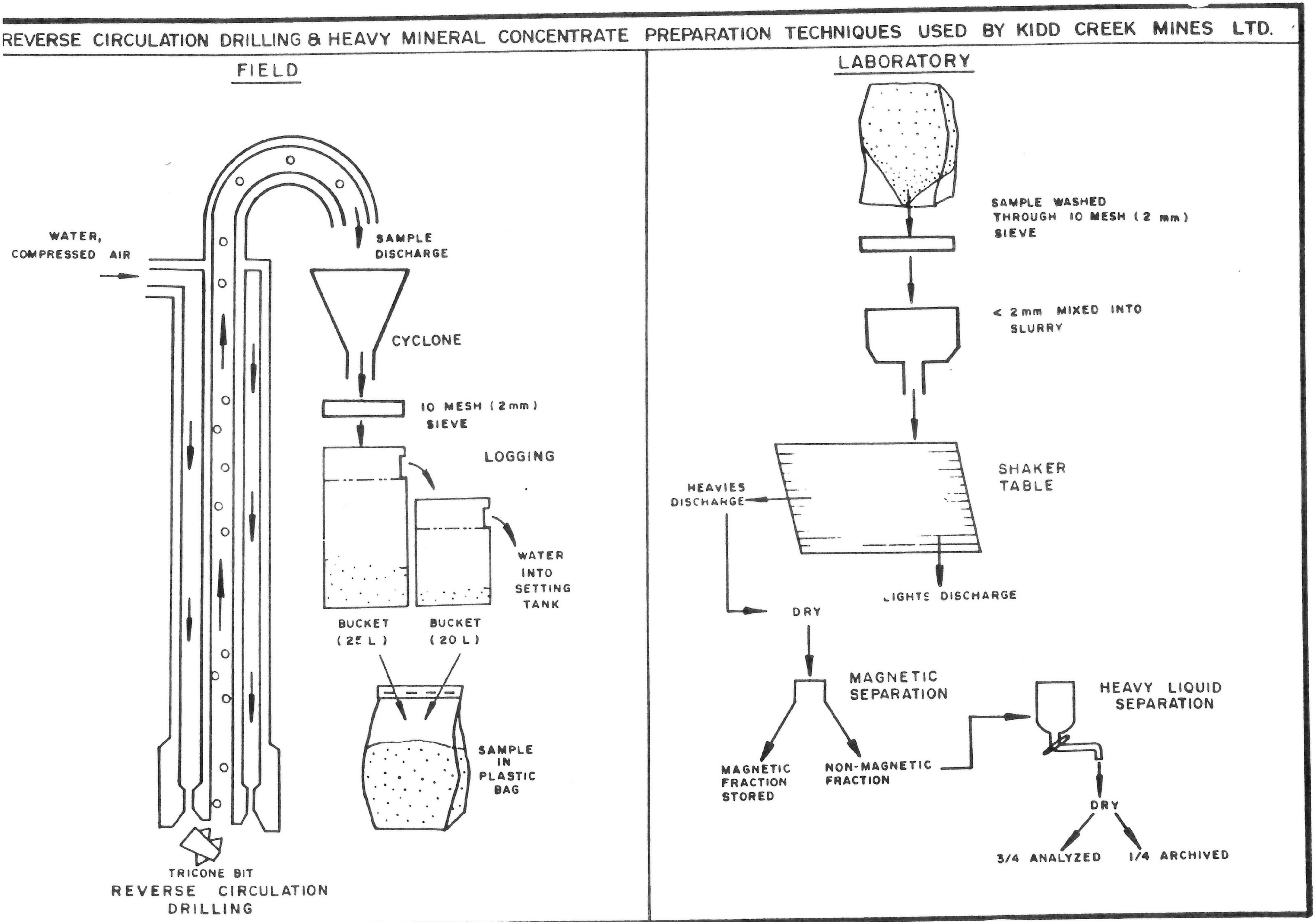


Figure 33. Reverse circulation drilling and heavy mineral concentrate preparation techniques used by Kidd

relationship between grain size, content of element and volume of material required to maintain specified precision. Sample splitters or coning and quartering methods should be used in dividing larger samples, and segregation of minerals should be avoided by thorough mixing.

From the above brief description, it should be clear that sample preparation is an important facet in the laboratory aspect of exploration geochemistry. The effects of improper grinding, splitting and other laboratory operations can result in errors which are devastating, sometimes reaching 100% or more. In large scale commercial operations, the preparation of samples is most likely to be the source of the delay in the reporting of results relative to any other part of the analytical operation.

It is sometimes more economical to do the sample preparation in the field, if possible, and then send only the prepared material to the laboratory. This also allows for much easier insertion of blind duplicate and reference control samples.

D) Analytical Techniques

Analyses of geochemical sample materials can be broken down into two major components: sample decomposition and extraction, sometimes including separation/isolation of the element to be determined; and, estimation of the concentration of the element (see Figure 21).

1) Decomposition and Separation

Many methods of extracting trace metals from rock, soil, sediment and other materials are used in geochemical exploration ([redacted]. The user must choose a method giving optimum contrast between anomalous and background values within the constraints of cost, time, equipment and subsequent analytical steps. In many geochemical surveys, contrast can be improved by selective extraction of only certain forms of the element, rather than the total content of the element.

The terms "total", "readily extractable", "hot extractable", "cold extractable" and similar expressions are widely used in geochemical exploration but have no well-defined meanings. "Total" frequently refers to decomposition by fusion or treatment by hot concentrated acid, which usually extracts 80-100% of heavy metals from most samples, but which may extract less than 50% from some minerals and types of samples. Such methods are better termed "near-total". Alternatively, "total" may refer to analyses by emission spectrography, X-ray fluorescence or neutron activation, or decomposition by HF combined with strong acids, which give essentially total (i.e. 99%+) metal content for most natural materials. "Hot extractable" generally refers to treatment with hot acid in concentrations of 0.1 - 1M. "Cold extractable" (contracted to cx, as in cxCu) generally refers to treatmnet with buffer solutions of pH 4-9, possibly combined with complexing

Table 11.

Classification of some decomposition techniques useful in exploration geochemistry

Decomposition	Reagents
Strong decompositions	
(1) Digestion with hot, usually concentrated, mineral acids	HNO_3, HCl, $HClO_4$, HF
(2) Fusions:	
acid fusions	$KHSO_4$, $K_2S_2O_7$
ammonium halide sublimations	NH_4I, NH_4Cl
alkaline fusions	Na_2CO_3, NaOH, $LiBO_3$
oxidative-alkali fusions	Na_2CO_3 or NaOH with KNO_3 or Na_2O_2
Partial decompositions	
(1) Non-selective decompositions:	
cold dilute mineral acids: e.g.	0.1-1.0 N HCl
buffers: e.g.	NH_4-citrate/NH_2OH HCl, pH 2-8
chelating agents: e.g.	0.05-0.25 M EDTA, pH 4-7
(2) Selective decompositions:	
(a) removal of exhangeable metals	NH_4-acetate; $MgCl_2$
(b) removal of organic matter	H_2O_2; NaOCl
(c) secondary iron and manganese oxides	Na-dithionite; hydrazine; hydroxylamine hydrochloride; NH_4-oxalate
(d) sulphides	$KClO_3$/HCl; ascorbic acid/H_2O_2; bromine

agents such as dithizone (diphenyldithiocarbazone) or EDTA (ethylene diamine tetraacetic acid), at room temperatures.

In view of the many possible treatments, no concise nomenclature seems possible, and the specific procedure used should be specified whenever possible and as closely as possible. It is essential that the geologist know exactly how the sample has been treated as this has definite implications at the data interpretation stage.

Both time and temperature, as well as chemical stability, affect the rate of decomposition of minerals in a sample being subjected to selective extraction or total dissolution.

The characteristic of some common methods of extraction and sample decomposition are reviewed below:

a) Volatilization

The sample may be decomposed by volatilization in the extreme heat of an electric discharge (emission spectrography), releasing essentially the total content of the element of interest, or in the more adjustable heat of an electric furnace (distillation of Hg) or induction furnace. The volatilized material may be determined directly by optical or other methods, or trapped by condensation or absorption in water for later determination.

b) Fusion

An effective method of attack is fusion of the sample with an inorganic salt that melts at a reasonably low temperature but, at the same time, is capable of a vigorous attack on the sample. Potassium bisulfate ($KHSO_4$) is acid; others are alkaline (Na_2CO_3) or oxidizing (Na_2O_2). Non-oxidizing fusions may <u>not</u> release metal from organic-rich materials.

c) Vigorous Acid Attack

Hot concentrated acids are widely used as agents for decomposing samples; HNO_3, $HClO_4$, HCl, H_2SO_4 and HF have all been used. An acid attack by relatively concentrated HNO_3, HCl, $HClO_4$ or mixtures of these with each other and other acids decomposes Fe and Mn-oxides, clay minerals, carbonates, some silicates especially olivine, but trace elements in pyroxenes and amphiboles are only partly released ([redacted]). Mixtures containing $HClO_4$ appear to release the highest proportion of trace elements, probably because of the high temperature attainable and the oxidizing effect of this acid. Use of $HClO_4$ requires prior destruction of readily oxidizable organic material either by roasting or oxidation by HNO_3 or other oxidizing agent to avoid explosions. Complete breakdown of silicates and most other common minerals is achieved with a combination of HF and other acid(s). In general, oxidizing acids are best for decomposing sulfides [redacted] and organic matter, but non-oxidizing acids are better for

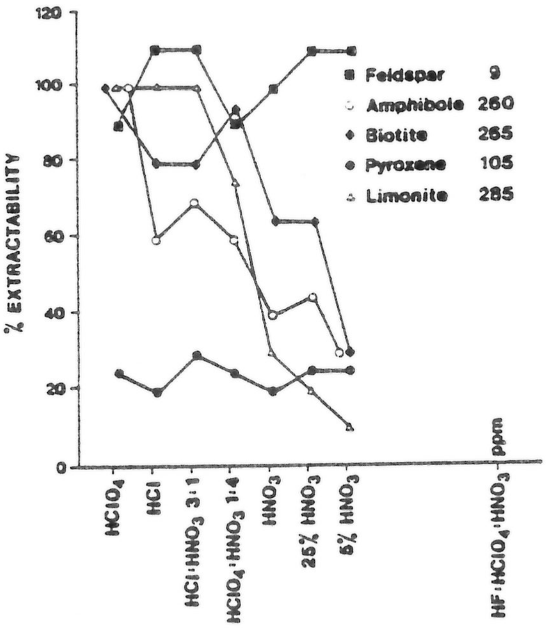


Figure 34. Variation in the extraction of Zn from some common rock-forming minerals with acid decompositions

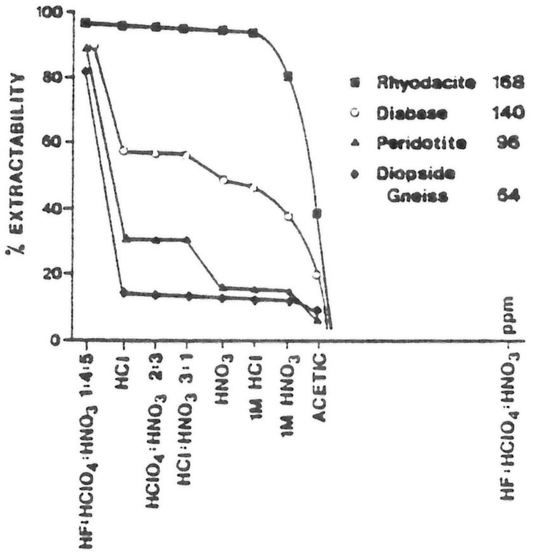


Figure 35. Variation in the extraction of Zn from dacite, diopside gneiss, diabase and peridotite with acid decompositions

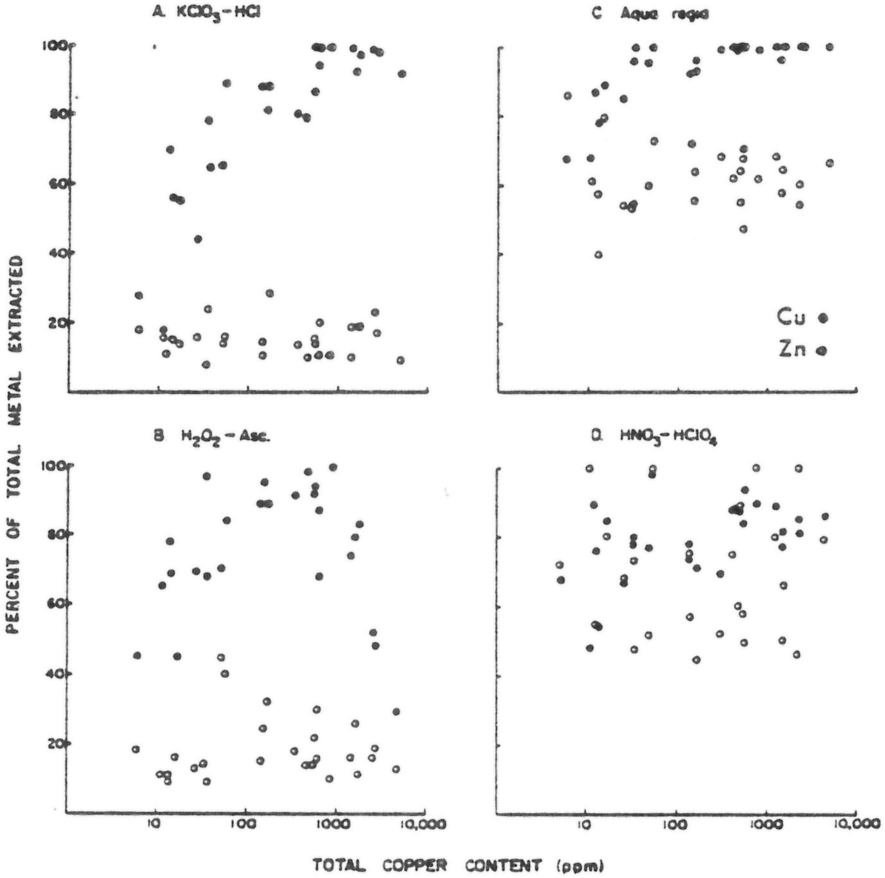


Figure 36. Sulphide-selective decompositions: relationships between extractable Cu and Zn, and total Cu content with potassium chlorate/hydrochloric acid, hydrogen peroxide/ascorbic acid, aqua regia and nitric acid/perchloric acid decompositions on bedrock samples associated with porphyry copper deposits, Guichon Batholith, British Columbia

dissolving Fe and Mn-oxides ([redacted]. Care must be taken not to lose elements by volatilization from concentrated acids; for instance, As, Sb, Cr, Se, Mn, Re, Ge, Mo and other elements can be lost during perchloric acid digestions. Loss of volatile metal-organic compounds during oxidation of organic matter is also possible.

d) Attack by Weak Aqueous Extractants

The trace metal content in exchange sites of clays and on the surfaces of colloidal particles can be released by displacing the trace metal. The H+ of dilute or weak acids, such as HCl, HNO_3 or acetic acid, acts as the major cation and displaces the trace metal. In near-neutral buffer solutions, such as Na-acetate, the high content of Na+ acts as the major cation. Organic complexing agents, such as citrate, tartrate, EDTA ([redacted]) and dithizone ([redacted]), decrease the content of free trace cation by complexing or chelating action and thereby promote release of the trace element. Associated alkali, H+ or other cations also aid the exchange. Some of these reagents also dissolve carbonates and other readily soluble minerals, but silicate lattices are little affected.

e) Oxidation - Reduction Agents

Hydroxylamine, dithionite, hydroquinone and oxalate act as selective reducing agents for Fe and Mn-oxides. In near-neutral solutions, these reagents

Table 12.

Influence of hydroxylamine hydrochloride on the extraction of heavy metals from stream sediments in relation to their manganese content[1]. Heavy metals determined by the dithizone field test.

Sample No.	Citrate-soluble heavy metals		Manganese
	with $NH_2OH \cdot HCl$	without $NH_2OH \cdot HCl$	
A-1046	900	17	150,000
738	550	17	80,000
1834	350	14	60,000
1914	450	25	60,000
628	225	11	45,000
653	140	27	45,000
1034	250	14	45,000
1037	180	17	45,000
736	140	22	30,000
1837	130	32	30,000
600	60	17	15,000
602	90	14	15,000
839	70	22	15,000
1917	32	9	12,000
598	70	17	11,250
1918	32	9	7,500
1915	27	20	4,000
1932	70	40	4,000
1916	9	4	1,500
1929	14	9	1,000
1934	11	5	1,000
1927	14	9	750
1931	9	7	500
1935	5	4	500
1936	4	3	250

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[1] Values in parts per million

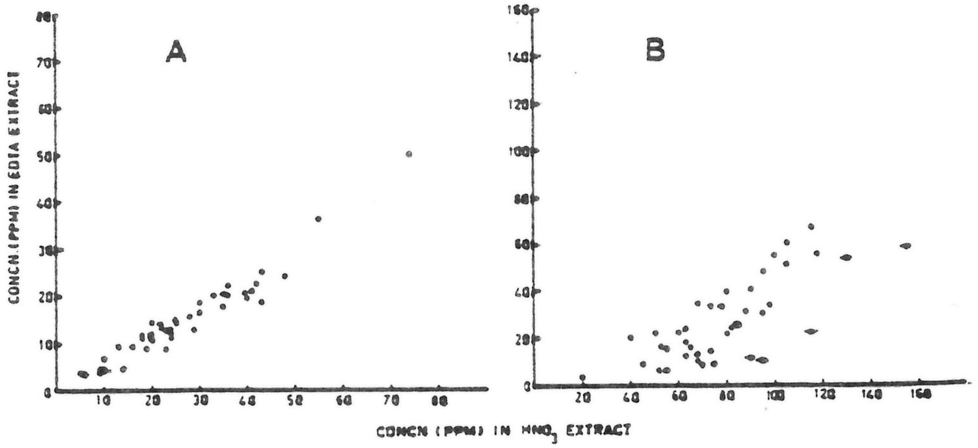


Figure 37. Analysis of lake sediments. A. EDTA-soluble Cu versus nitric acid-soluble Cu. B. EDTA-soluble Zn versus nitric acid-soluble Zn. ◆= samples containing ferromanganese nodules give abnormally high Zn concentrations with the acid decomposition

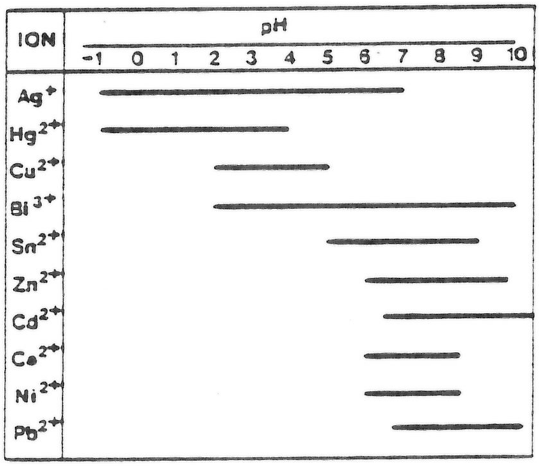


Figure 38. Optimum pH ranges for formation of metal-dithizone complexes

have little effect on the lattices of clays and other silicates. Similarly, hydrogen peroxide, hypochlorite, chlorite and nitric acid act as oxidizing agents for sulfides and organic material. Ashing or treatment with strong acids may be necessary to extract metal chelated by organic matter.

Once the trace element under study has been released from the sample, it may be necessary to separate it from interfering elements liberated from the sample at the same time. Separation is especially needed prior to most colourimetric methods but is not usually required before determination by atomic absorption. The process of separation may also aid by concentrating the element in the separate phase, thus increasing the effective sensitivity of the overall method. Where the element is present in extremely low concentrations, as is often the case in natural waters, enrichment of the element is often necessary for its determination.

Common separation techniques used include solvent extraction, ion-exchange and precipitation methods.

2) Estimation Techniques

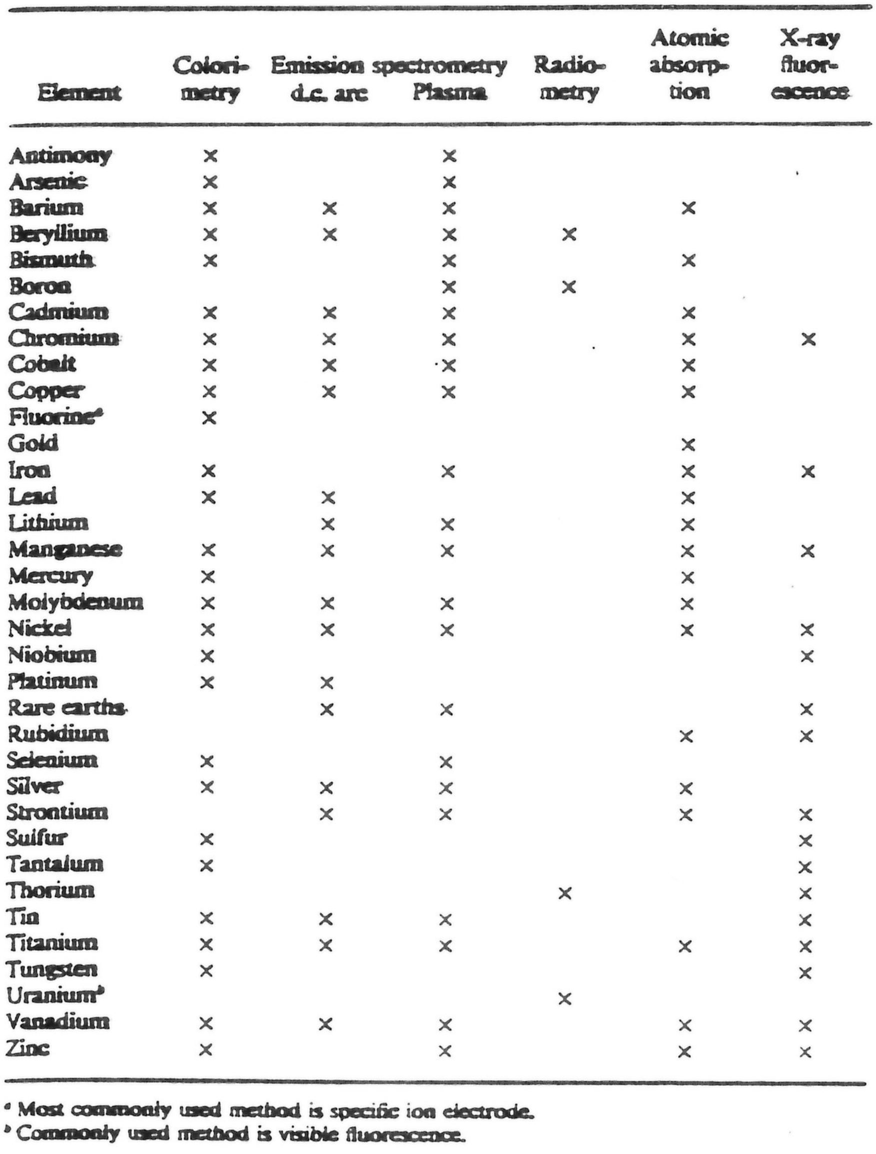
A brief review of the principal methods of estimation and the elements for which they are best suited along with some of the advantages and disadvantages of these methods in geochemical exploration are reviewed [redacted]:

Table 13.
Evaluation of performance of analytical methods commonly used in exploration geochemistry

Method	Equipment Cost ($1,000)	Precision	Freedom from interferences	Multi-element capability	Determinations per man day	Solid samples	Comments
1. Colourimetry	1	poor-good	variable	no	20-100	no	very simple: adaptable to field use; special reagents needed for each element
2. Atomic absorption	20	good	very good	no	500	no	easy to set-up and operate; several elements can be determined on same solution; special methods for Hg, As, Te, Se; dilutions required for high concentrations
3. Emission spectroscopy							
visual comparison	40	very poor	very poor	yes	500	yes	simple robust equipment: requires comparator and darkoom; results semi-quantitative
direct reader	100 - 200	poor	poor	yes	1000	yes	sophisticated equipment: requires experienced analyst to set-up and supervise operations; requires dedicated computer or access to computer
ICP-direct reader	100 - 200	good	variable	yes	1000	yes	
4. X-ray fluorescence							
wavelength dispersive	300	good	good	yes	1000	yes	sophisticated equipment; requires supervision by a skilled analyst; dedicated computer or access to computer; very simple sample preparation
energy dispersive	100	good (?)	good (?)	yes	500	yes	

Table 14.

Methods of estimation and minor elements for which they are commonly used.



Element	Colorimetry	Emission spectrometry		Radiometry	Atomic absorption	X-ray fluorescence
		d.c. arc	Plasma			
Antimony	×		×			
Arsenic	×		×			
Barium	×	×	×		×	
Beryllium	×	×	×	×		
Bismuth	×		×		×	
Boron			×	×		
Cadmium	×	×	×		×	
Chromium	×	×	×		×	×
Cobalt	×	×	×		×	
Copper	×	×	×		×	
Fluorine[a]	×					
Gold					×	
Iron	×		×		×	×
Lead	×	×			×	
Lithium		×	×		×	
Manganese	×	×	×		×	×
Mercury	×				×	
Molybdenum	×	×	×		×	
Nickel	×	×	×		×	×
Niobium	×					×
Platinum	×	×				
Rare earths		×	×			×
Rubidium					×	×
Selenium	×		×			
Silver	×	×	×		×	
Strontium		×	×		×	×
Sulfur	×					×
Tantalum	×					×
Thorium				×		×
Tin	×	×	×			×
Titanium	×	×	×		×	×
Tungsten	×					×
Uranium[b]				×		
Vanadium	×	×	×		×	×
Zinc	×		×		×	×

[a] Most commonly used method is specific ion electrode.
[b] Commonly used method is visible fluorescence.

a) Colourimetry

The formation of coloured compounds in solution by reaction of an element with a specific chemical reagent is the basis of colourimetry. Quantitative determination of the element is possible if the intensity of the colour is proportional to the concentration of the coloured compound. Estimation of the intensity or hue of the colour, in the coloured solution, can be made by visual comparison or instrumentally by measurement of the absorption of the complementary colour (spectrophotometry) as light is transmitted through the solution [redacted]. A few colourimetric reagents form coloured compounds only with one element, but most react with several elements, so preliminary exclusion of interfering elements by complexing or separation is usually required. Very commonly, the coloured complex is extracted from aqueous solution into an organic solvent, thereby concentrating it and separating it from many interferences. Dithizone is a common colourimetric reagent which can be used to separate and estimate many elements by varying the pH of extraction and adding complexing agents for unwanted elements (Figure 38). The advantages of colourimetry in geochemical exploration are the simplicity, low cost and portability of the equipment, and the ease of training unskilled personnel in its operation. The

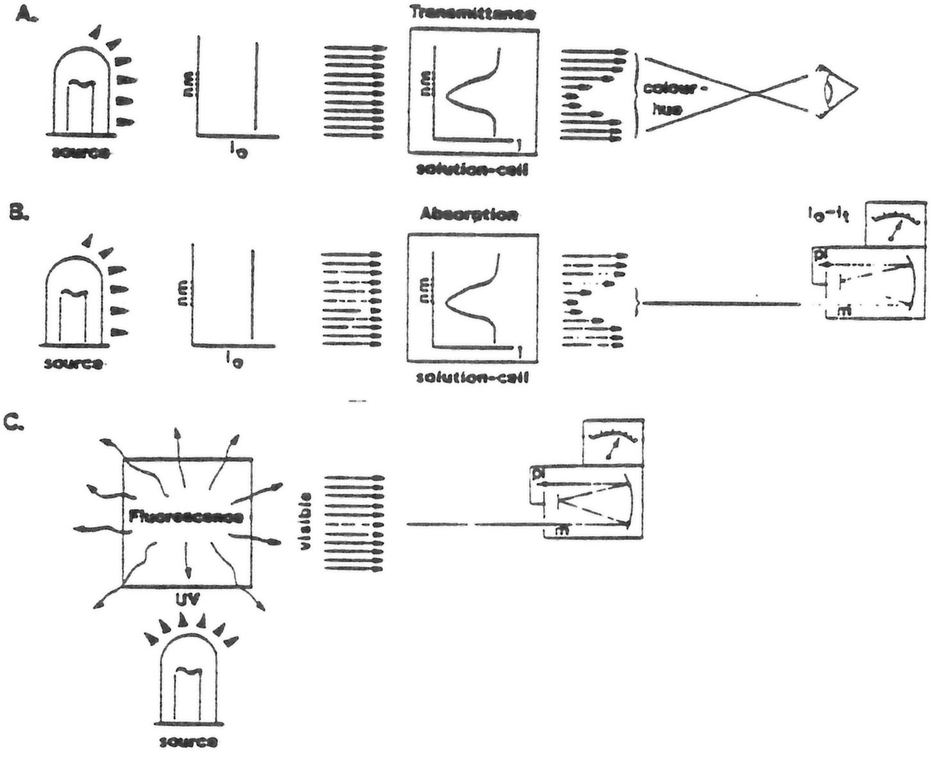


Figure 39. Idealized representations of (A) colourimetry, (B) spectrophotometry, (C) fluorimetry. I_0 and I_t = intensity of incident and transmitted light, respectively

disadvantages are the inability to determine more than one element at a time and the sensitivity of many reagents to interferences and aberrant chemical conditions.

b) Fluorimetry

When a fluorescent substance is exposed to ultraviolet radiation, it emits visible light at a longer wavelength than the excitation source [redacted]. Intensity of the fluorescence is proportional to concentration of the fluorescor and can be estimated visually, by comparison to standards or measured in a fluorimeter.

In the laboratory, fluorescence of the uranyl ion, which is particularly intense in the presence of fluoride, provides a sensitive method for estimation of U in discs prepared by fusing the sample with a $K_2CO_3/Na_2CO_3/NaF$ flux. Quenching agents, especially Mn [redacted] but also Cr, Co, Ni, Fe, Ag, Pb, Pt and others, suppress the fluorescence of U. However, providing the sample to flux ratio is kept low and fusion conditions are carefully controlled, the method is adequate for many purposes and has the advantage of simplicity. Despite the additional steps involved, many laboratories prefer to avoid potnetial quenching problems by separating U from other elements by solvent extraction or precipitating the manganese out of the solution.

Table 15.

Comparison of uranium content of sediments determined by fluorimetry, with and without solvent extraction, after digestion with 4 N nitric acid.

Uranium content (ppm)		Mn (ppm)
direct fluorimetry	with solvent extraction	
58	282	238
1	3	118
2	5.5	226
5	16	954
0.2	1.0	5,200
0.5	1.1	440
0.2	3.9	4,300
16.8	62.5	240
0.7	6.8	3,850
1.3	11.4	300
8.0	18.8	720
161.0	435.0	665
0.1	10.7	1,640
31.2	105.0	680
0.8	370.0	5,400
0.1	160.0	405,000

Recently, direct measurement of U in waters has been described using laser-stimulated uranyl ion fluorescence. The UV laser developed by Scintrex (UA3 Analyzer) causes fluorescence of both natural dissolved organics and uranyl ions ([redacted]. However, the fluorescence of the latter persists slightly longer than that of the organics when the laser is switched off. Consequently, by modulating the laser and tuning the detector, it is possible to measure only the uranyl ion fluorescence. A proprietary solution is added to the sample to adjust pH (5-7) and ensure U is present in the uranyl form; similar results can be obtained by addition of a sodium hexametaphosphate solution. Waters should be analyzed as soon as possible after collection and without acid preservation.

c) Atomic Absorption Spectrophotometry (AAS)

Atomic absorption spectrophotometric analysis involves chemical extraction or concentration of metallic compounds into a solution matrix, introduction of the solution into a high temperature flame (i.e. oxidizing air/acetylene ≈ 2200°C or reducing nitrous oxide/acetylene ≈ 2955°C) which vaporizes the sample solution and breaks down the metallic compounds into their constituent atoms, and the excitation of the atoms by absorption of radiant energy ([redacted]. The radiant energy, a sharp spectral line corresponding to the element to be analyzed, is generated in a hollow

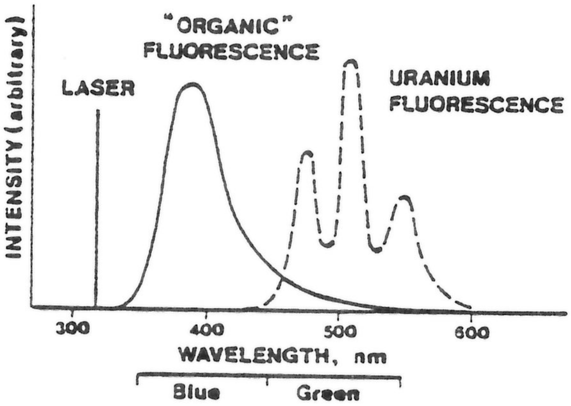


Figure 40. Direct determination of U in solution by laser-induced fluorescence. As well as being at a longer wavelength than the fluorescence due to organic matter, the fluorescence of the uranyl ion persists longer after the laser is turned off.

cathode source lamp and passed through the atomized sample. The wavelength absorbed is specific to the element being measured, and the proportion of light absorbed is a measure of the concentration of the element.

Variations on the method of vaporizing the sample solution involve resistance-heated furnaces and electrothermal furnaces ([redacted] where direct vaporization of solids or liquid concentrates/ extractions into the light path allows more efficient use of the sample (i.e. small volume) and generally better sensitivities. A method used for atomization of such elements as As, Bi, Sb, Se, Sn and Te is the hydride generating system and furnace ([redacted]. In addition, estimation of Hg can be carried out by flameless atomic absorption spectrophotometry after its release from samples either by pyrolysis or acid digestion followed by reduction in solution to elemental Hg ([redacted].

Freedom from interferences is often cited as one of the principal advantages of AAS. Nevertheless, if samples and standard solutions differ in bulk composition, a variety of interferences can cause enhancement or depression of the signal unrelated to the actual concentration of the element being measured. Principal sources of interferences and some remedial methods are summarized in [redacted]

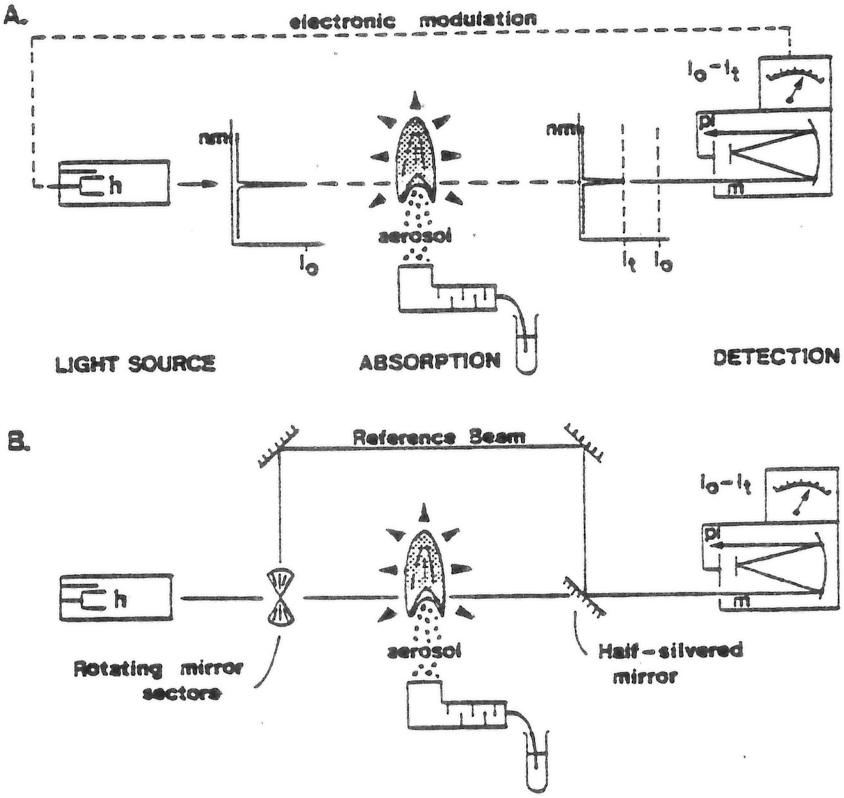


Figure 41. Schematic diagram of atomic absorption spectrophotometers: (A) single-beam and (B) a double-beam instrument. h = hollow cathode light source; m = monochromator; and p = photomultiplier. I_0 is the intensity of the signal from the light source and I_t its intensity after absorption by analyte atoms in the flame.

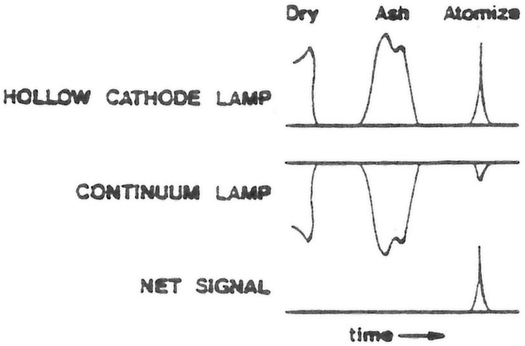


Figure 42. Typical absorption curves for the dry, char and atomize stages of electrothermal atomizers. Subtraction of non-atomic absorption, measured with a continuum source, from total absorption, measured with the hollow cathode lamp, gives the signal due to the analyte. During drying and charring, smoke and vapour can give large non-atomic absorption signals.

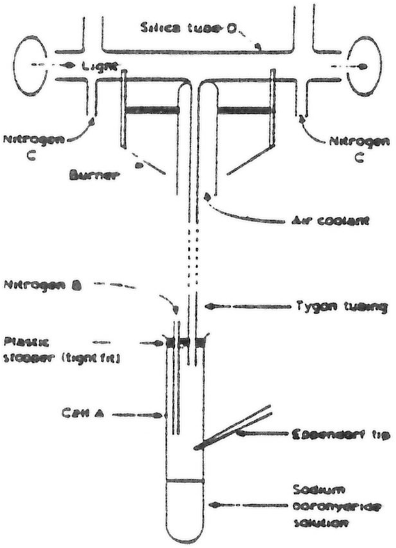


Figure 43. Apparatus for AAS determination of elements forming gaseous hydrides. A 1-ul volume of sample is injected into the borohydride solution in the cell. Gaseous hydrides are then swept by a flow of nitrogen into the silica absorption cell (D) heated by the air/acetylene flame of a triple-slot burner.

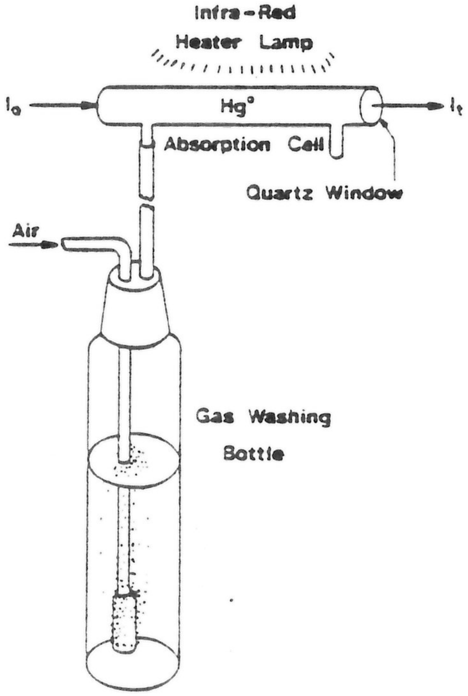


Figure 44. Cold vapour generation and determination of Hg by AAS. In the gas washing bottle, Hg^{2+} is reduced to Hg° with Sn^{2+} and then swept into the absorption cell by a stream of air. The IR heater lamp prevents condensation of water vapour in the cell.

Table 16.

Some interferences in the determination of trace elements in geological matrices by flame atomic absorption spectrophotometry

Element[1]	Interference[2]	Comments
Ag	B	background correction
Ba*	C, I	suppression by Si, Al and P - add oxine or NH_4Cl; enhancement by alkalies and alkali earths - add K radiation buffer
Be*	C	suppression by Al
Cd, Co	B	background correction
Cr	C	suppression by Fe, Na and K; enhancement by Al, Mg, Ca - interference and sensitivity reduced in N_2O/C_2H_2 flame
Mo*	C	suppression by alkalies, Ca, Fe - add up to 1000 ug/ml Al
Ni, Pb	B	background correction
Rb	I	add K radiation buffer
Sr*	C, I	add K radiation buffer and La releasing agent
V*	C	suppression by Fe and Ti - add 1000 ug/ml Al
Zr*	C	add NH_4F

[1] Determined in clean air/acetylene flame except (*) in nitrous oxide/acetylene flame

[2] B = background absorption; C = chemical (suppression); I = ionization (enhancement)

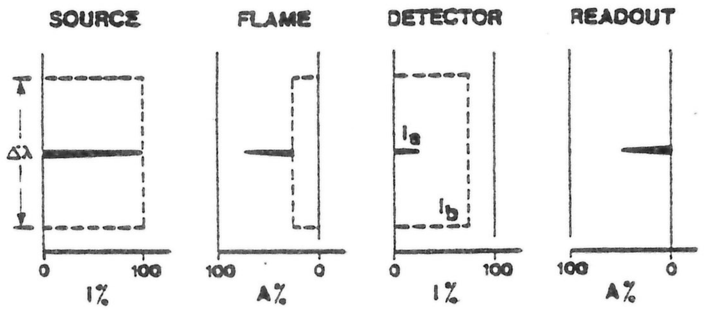


Figure 45. Background correction using a continuum source. The profile of the atomic absorption line is shown in solid black and the continuum is represented, over a slit width of $\Delta\lambda$, as the area within the dashed line. At the light source the emission intensity of the atomic line and continuum are balanced at 100%. In the flame atomic absorption is superimposed on background absorption so that the intensities reaching the detector are I_a and I_b, respectively. The readout displays these intensities as a net signal equal to $(100 - I_a) - (100 - I_b)$.

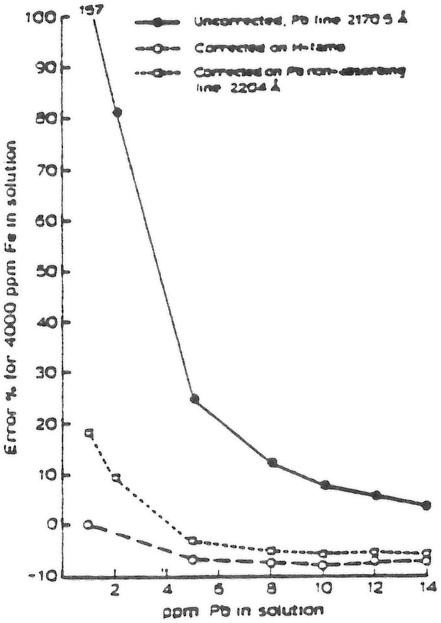


Figure 46. Errors in uncorrected and background-corrected measurement of Pb in the presence of 4,000 ppm Fe

Atomic absorption, mainly using dissolved samples, has in recent years become the most widely used analytical method in exploration geochemistry because of the low detection limits for most elements of interest, the specificity for individual elements [redacted], the opportunity to determine several elements on one solution and the relatively inexpensive and simple equipment required. A minor disadvantage for most conventional equipment is the limitation to analyzing one element at a time. Recent experiments suggest that selective volatilization from solid samples in furnaces provides very low detection limits for some elements, allows inferences on the form of elements in samples and has potential advantages analogous to other methods of partial extraction.

d) Emission Spectroscopy (ES)

Rapid, virtually simultaneous multi-element analysis with minimal sample pre-treatment offers obvious advantages, particularly for regional reconnaissance programmes in which it is desirable to determine as wide a range of elements as possible [redacted]. Hence, despite greater capital cost, complexity of equipment and need for skilled personnel compared to single element methods, there has been a continuing interest in emission techniques based on sample excitation in D.C.-arc and, more recently, inductively coupled plasma (ICP) and direct current

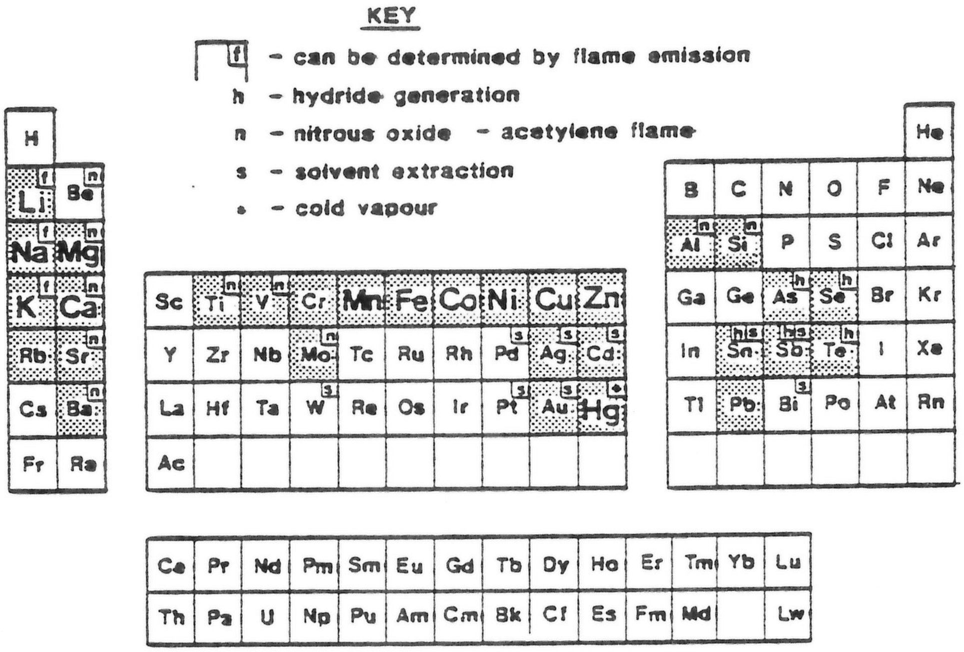


Figure 47. Analysis of exploration samples by AAS. Elements most suitable for determination by AAS shown in stipple; bold face letters indicate that the concentration of the element can normally be estimated without difficulty after sample decomposition with strong acids. Small letters indicate that special operating conditions are required or recommended as shown in the key.

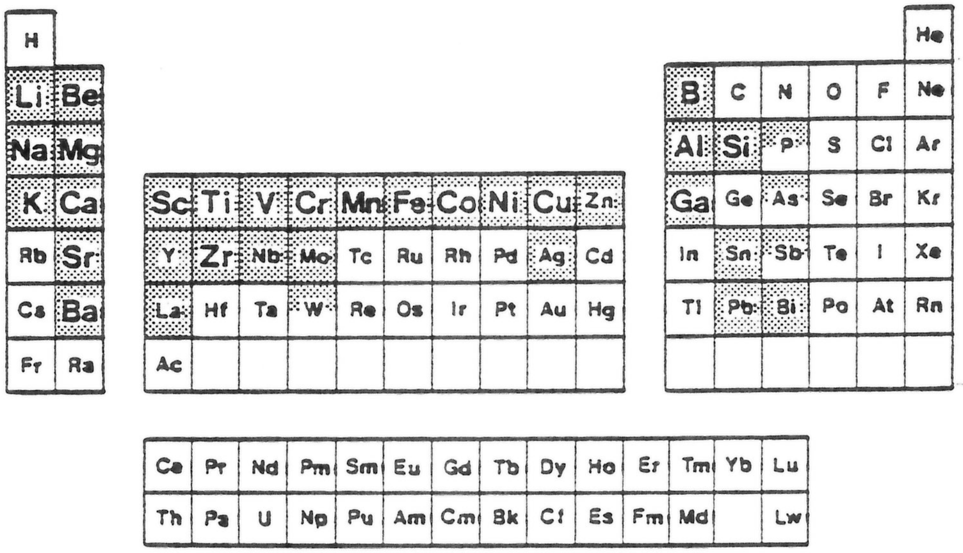
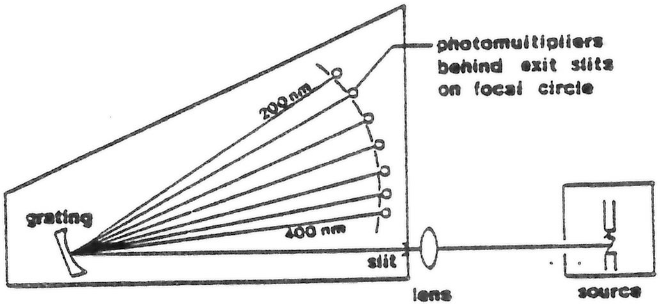


Figure 48. Analysis of exploration samples by D.C.-ES. Emission lines of elements in bold face and stipple are almost invariably present in the D.C.-arc spectra of geochemical samples: elements in stipple are often visible and those in half-stipple are occasionally visible. Remaining elements either cannot be determined by ES or are only very rarely seen in emission spectra of rocks, soils and sediments.

plasma (DCP) sources ([redacted]. Almost all elements, when vaporized and ionized in the intense heat of an electric discharge or other source of energy, emit radiation of characteristic wavelengths in the visible and ultraviolet range as a result of electrons refilling the outer electron orbitals. The spectra emitted by the excited atoms can be either recorded photographically or measured instantaneously with photomultipliers in direct reading spectrometers. The element can be identified by the wavelength emitted, and the concentration of the element can be determined by the intensity of the light. In the past, the main source of energy has been a D.C. or other arc in which a small amount of sample was burned as a powder (10-50 mg) or occasionally as a liquid (uL). Recently, plasmas (gases highly excited by radio-frequency induction or other means) have been used as an energy source, with the sample introduced as a solution.

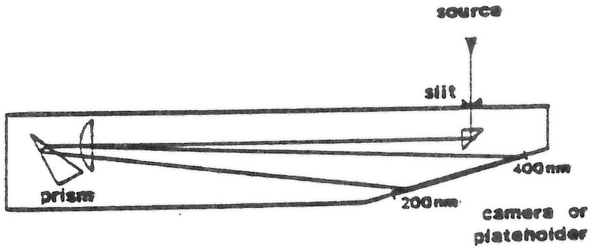
i) D.C.-Arc Emission Spectroscopy (D.C.-ES)

The excitation source is the D.C.-arc, with the lower sample holding electrode as the anode. Arc currents needed are 10-15A but should be capable of up to 30A. In D.C.-arc, the sample powder is volatilized directly. Sample composition has a considerable influence on arc temperature, volatilization rate, and distribution of atom and ion excitation states. These variations must be controlled, with spectroscopic

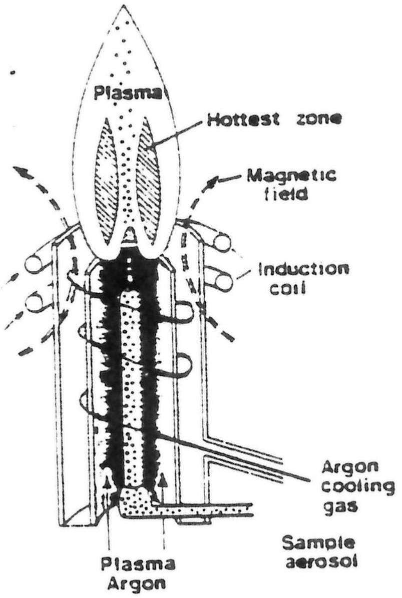


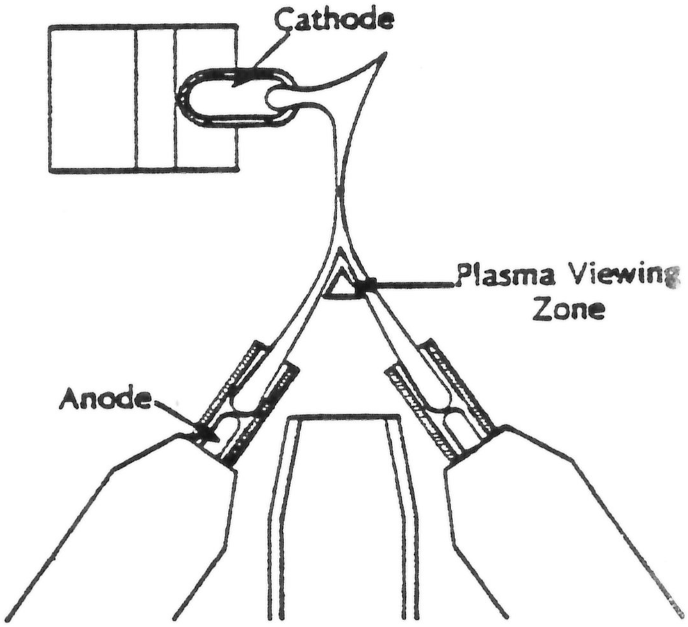
c) D.C.-arc,

a) DIRECT READING SPECTROGRAPH WITH GRATING



b) PHOTOGRAPHIC SPECTROGRAPH WITH PRISM





d) Inductively coupled plasma

e) Direct current plasma

Figure 49. Schematic diagrams of (a) direct reading and (b) photographic spectrographs with (c) D.C.-arc, (d) ICP and (e) DCP excitation sources

buffers ($LiCO_3$, NaCl, Na_2CO_3 and NaF together with graphite) for matrix effects, and monitored and corrected for using internal spectroscopic standards.

To obtain quantitative results based on photographically recorded spectral lines their intensities must be measured using a densitometer and corrected for emulsion characteristics. This is generally too time-consuming for routine analysis. Concentrations are therefore usually estimated by visual comparison to standard films prepared under identical conditions. This, together with the inherent noisiness of the D.C.-arc and the sampling problems associated with the small quantities of material (10-50 mg) taken for analysis, makes it difficult to obtain results that are better than semi-quantitative.

In the direct-reading spectrometer, the photographic plate is replaced by photomultipliers connected to voltmeters, which convert light intensity to an electronic readout, hooked to a computer programmed to correct for background, matrix effects and spectral interferences. With suitable internal standards and matrix corrections based on simultaneous determination of the bulk chemical composition of samples, the D.C.-arc direct reading spectrometer can provide more reliable results than semi-quantitative photographic procedures.

ii) Plasma Emission Spectroscopy (ICP and DCP)

Plasmas are masses of gas sufficiently ionized for this to have a significant effect on their properties. Most important for their use as emission sources, large quantities of electrical energy can be pumped into them giving temperatures much higher (7-10,000°K) than those attainable in flames or arcs. In contrast to D.C.-arc spectroscopy, the sample is usually introduced into the plasma in solution: the technique therefore has all the advantages and disadvantages associated with dissolution of geochemical samples.

The advantages of emission spectroscopy are: (1) the ability to excite the lines of a large number of elements; (2) high sensitivity; (3) good stability; (4) freedom from interferences; (5) reproducibility in the introduction of samples; and (6) convenience of operation. Particularly with regard to (3), (4) and (5), the D.C.-arc is not an ideal source: the inductively coupled plasma (ICP) is now attracting considerable attention as an alternative source. The disadvantages are the high cost of equipment and the need for a highly trained operator. Poor reducibility has also been a problem with conventional electric arc sources.

e) X-Ray Fluorescence Spectrometry (XRF)

X-Rays, which occupy the electromagnetic spectrum between 0.01-10 nm, are the most energetic form of non-nuclear radiation. When a sample is bombarded by electrons, secondary X-rays are emitted at wavelengths (or energies) and intensities that are determined by the elemental composition of the sample. Measurement of the intensity of this secondary, characteristic radiation is the basis of X-ray fluorescence [redacted]

In conventional X-ray spectrometers, the sample is the target for primary X-rays generated in an X-ray tube requiring a stable, high voltage power supply. Where this is impractical, as in portable field instruments, radio-isotopes can be used as a primary radiation source. The characteristic radiation of the element to be determined is isolated from other secondary X-rays on the basis of its wavelength or energy and its intensity measured. For elements lighter than Fe (atomic number Z = 26), the characteristic radiation is strongly absorbed by air and it becomes necessary to mount the sample and detector in a vacuum chamber [redacted].

XRF, which has found wide acceptance for determination of the major constituents of rocks, is also capable of providing excellent data for many trace elements in geochemical matrices [redacted] Sample preparation can be extremely simple. After fine grinding (i.e. < 50 μm), the sample can be poured directly into a sample holder for irradiation. It can

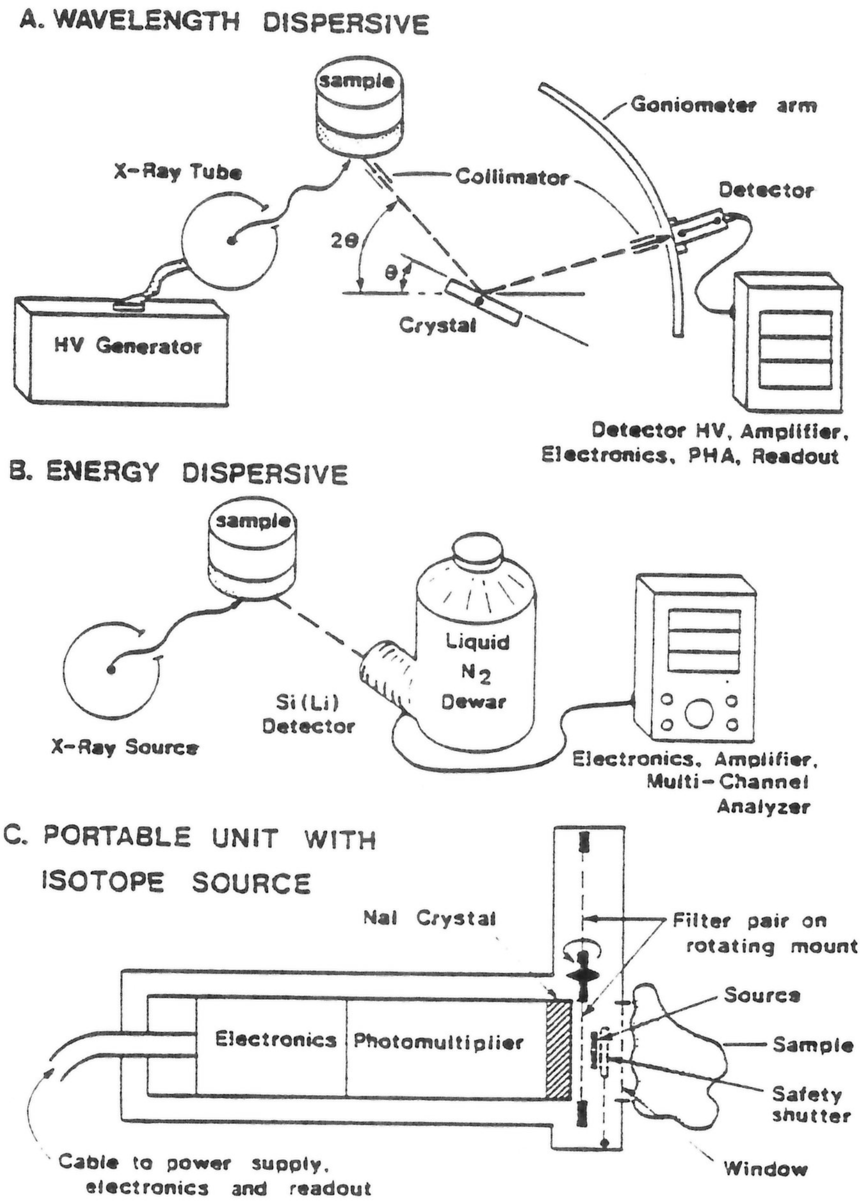


Figure 50. X-ray spectrometers. A. Wavelength dispersive. B. Energy dispersive. C. A portable instrument with an isotope source and filters

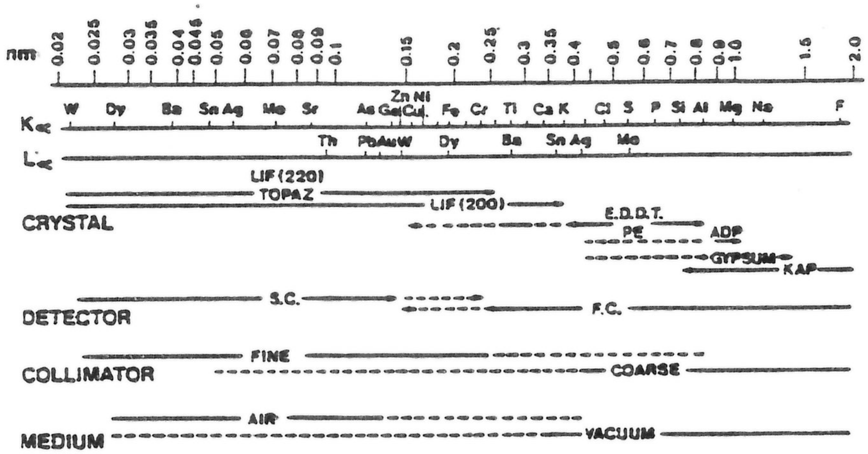


Figure 51. General operating conditions with a wavelength-dispersive X-ray spectrometer

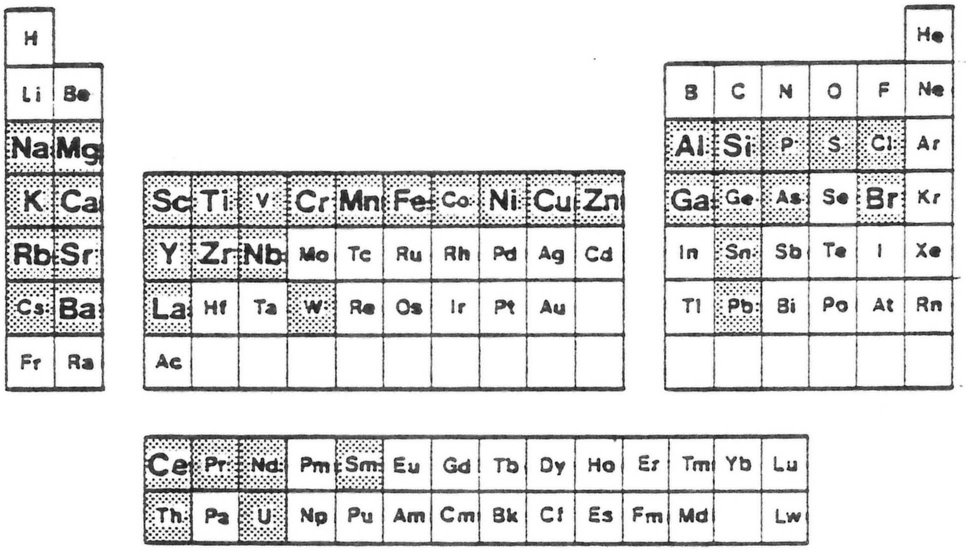


Figure 52. Analysis of exploration samples by XRF. concentrations of elements in bold face and stipple can be estimated by XRF in most samples. Concentrations of elements in stipple only are usually close to or below their detection limits; they will only be measurable in samples with above average contents.

also be mixed with a binding agent placed into a holder and a pressed pellet produced for irradiation. However, because of the wide compositional variations of geochemical samples and differential excitation of different components of individual samples as a result of textural and mineralogical effects, it is only possible to obtain reliable results if sample preparation is designed to minimize textural variations and if corrections are made for matrix effects and for mass absorption differences between samples and standards. To reduce these problems, fusion of the sample to give a homogeneous glass disc, which is ground up mixed with a binding agent and pressed into pellets, is used where accurate whole rock analyses are required (i.e. WRDB).

Compared to ES, colourimetry and AAS, application of XRF in exploration laboratories has been relatively limited. This perhaps reflects the higher capital cost of the conventional wavelength-dispersive X-ray spectrometer, its somewhat poorer detection limits for many of the elements of interest and the need to correct data for matrix effects. Recent advances in energy-dispersive (or non-dispersive) X-ray spectrometry have reduced capital costs for simultaneous multi-element determinations. This should promote a re-evaluation of the potential applications of X-rays in geochemical exploration.

f) Neutron Activation (NAA)

The elements U, Th and K and some of their decay products may be detected and measured by their natural radioactivity using scintillometers. Non-radioactive elements can be converted into radioactive elements by bombardment with neutrons or other atomic particles (neutron-activation analysis). The best source of the high density neutron flux required for this purpose is a nuclear reactor. Bombardment induces the formation of radioactive isotopes peculiar to the elements in the sample. As these isotopes decay, they emit characteristic gamma radiation which is directly proportional to the elemental concentrations. Measurement of specific spectral intensities allows a quantitative evaluation of specific elemental concentrations. The most significant benefit neutron activation offers over other analytical methods is the simplicity of sample treatment prior to analysis. In most cases, all that is required is the reduction of the sample to a particle size (having regard for the rules of sampling) suitable for encapsulation. This is true for such elements as U, Th, W, Ta, As, Sb, Se, V, Sc and rare earths where detection limits are typically in the low to sub ppm range. Elimination of the usual multi-step, operator-sensitive, chemical pre-treatment common to other analytical techniques has a dramatic effect on the reliability of the final data.

A few elements, notably gold and the platinum group elements (PGE's), do require some pre-treatment. The detection limits attainable are, however, far superior to those achieved by alternate methods, and in the case of the PGE's, all six elements of this group are determinable simultaneously, something that has previously not been possible. Preconcentration methods used for these elements involve some form of fire assay collection using a sub-sample of 20-50 grams. The heterogeneity problems common to gold and the PGE's are consequently lessened. Disadvantages of neutron activation are the high cost of the equipment and general unavailability of a neutron source, and the need for highly-trained operators.

g) Electroanalytical Methods (Specific Ion Electrodes-SIE)

Measurements of electrical potentials and electrical currents in solutions have several applications in analyzing for trace elements. Measurement of pH by the potential of a glass electrode and Eh by potential of a platinum electrode are the best known procedures of this group. Analogous methods using electrodes sensitive to F^-, Cl^{-1}, Cu^{2+} and other ions are in use. Specific-ion electrodes are easy to use and have sensitivities generally less than 1 ppm, but they can be subject to interferences from other ions. The electrodes measure the chemical activity of the ions rather than their total concentration in solution, so that careful calibration and selection of the chemical medium are important. The specificity and simplicity of specific-ion electrodes are likely to lead to their more widespread use.

Other electroanalytical methods include the measurement of dissolved oxygen in water by electrical measurement of the current derived from decomposition of oxygen diffusing through a membrane selectively permeable to oxygen, and measurement of conductivity of solutions as a means of estimating the content of ionized solutes in water.

From the descriptions and discussions of the various analytical methods, one fact should have emerged, and that is that no one method can satisfy all exploration requirements. Also, it should be clear that considering the expense of the various analytical instruments plus the necessity for specialists to operate the more sophisticated types, few laboratories are completely equipped to determine all elements of potential importance and at the necessary abundance levels. Notwithstanding the other factors which enter into the selection of the best analytical method, one which weighs very heavily is the lower limit of detection.

Of great importance to those engaged in exploration geochemistry is the selection of the best method to use for the analysis of a specific element. Most persons concerned with the geological or collection aspects of exploration geochemistry tend to avoid the analytical aspects by sending samples to commercial laboratories, simply indicating the element(s) of interest and leaving the decision-making to the analyst. Only occasionally will they discuss their problems with the analyst who might then be in a better position to obtain the information of most value to the geologist. He would, for instance, try to determine whether a quantitaive, semi-quantitative or only a qualitative analysis is needed; what part of the sample (size fraction) should be analyzed; what interferences are likely to occur (if any); if a total or partial analysis is needed; the number of samples to be analyzed as this might have a bearing on the method selected; how rapidly the results are really needed; the problems, if any, to be encountered in sample preparation and their effect on the results; and, finally, the accuracy and precision needed. Then, on the basis of all this information, he would be able to select the best analytical method. In practical situations, the lack of liaison between sample submitters and analysts has always been, and remains, a serious problem.

E) Analytical Data Formatting

Laboratory data are being received by Kidd in many different forms at present. There is a need to standardize the format of analytical data reporting (i.e. the same variables should be reported similarly, in the same columns with the same number of decimal places, detection limit values should be reported as one-half the detection limit, etc.). This will make data handling and computerization much easier. The data can be reported on standard lab sheets or on tape under specified fixed format.

Recording of detection limit values (D.L.) can also be a problem. A "Not Analyzed", usually recorded as N.A., indicates the sample was not analyzed and accordingly no value, especially not zero (0), should be recorded. If NIL or < 2, <5, etc. are reported, then the level of the parameter measured was less than the detection limit of the analytical method used. The best method is to record approximately one-half the detection limit (i.e.<2 = 1,<5 = 3; for NIL, the detection limit will have to be determined and one-half that value recorded). Never, never use a value of zero (0) as it is geochemically, and in many instances statistically, meaningless. Note that some computer programs will not accept zero (0) as a valid number.

F) Laboratories

Kidd's dealings with the commercial laboratories currently involve each project geologist independently making his own arrangements with one or a number of these labs to carry out his analytical work [redacted] This has contributed to some confusion at the labs as to which samples belong to or come from whom at Kidd, assigning priorities to Kidd's work when one or more project geologist is using a given lab and, undoubtedly to a certain extent, poor turn around time. Perhaps it is time we tried to co-ordinate our use of the commercial laboratories. It may prove less time consuming, less trouble and result in a better turn around time and lower overall analytical costs. I have attempted to estimate our overall analytical requirements for the 1983 field season in terms of number and types of samples to be collected, preparation needed, elements to be analyzed and analytical techniques to be used [redacted]. Perhaps we should start to use the overall weight of our total analytical requirements (total dollars to be spent) to shop around at the various commercial laboratories to obtain lower costs for a given analytical method and also to get better turn around time.

GEOCHEMICAL DATA INTERPRETATION AND MANAGEMENT

From the discussion so far it should be clear that geologists and geochemists do not use geochemistry to search for ore directly but rather to indicate geochemical anomalies. The decision as to the true meaning of the geochemical data and resultant anomalies is probably the most difficult part of exploration geochemistry. One of the questions often asked of geochemists is, "What do these high values mean?". Unfortunately, there is no simple answer to the question, nor is there a guaranteed way to correctly, and unequivocally, interpret the results of a geochemical survey.

Table 17.

Commercial laboratories used by Kidd Creek Mines Ltd., Exploration Division in 1982 (based on 14 of 19 returned questionnaires)

1. Acme Laboratories, Vancouver, B.C.
2. Bondar-Clegg Labs, Vancouver, B.C.
3. Min-En Labs, Vancouver, B.C.
4. Chemex (Alberta) Labs, Calgary, Alberta
5. X-Ray Assay Labs, Toronto, Ontario
6. Assayers (Ontario) Ltd. Labs, Toronto, Ontario
7. Nuclear Activation Services Labs, Hamilton, Ontario
8. Bell White Analytical Labs, Haileybury, Ontario
9. Bondar-Clegg Labs, Ottawa, Ontario
10. Atlantic Industrial Research Institute Labs, Halifax, Nova Scotia
11. OceanChem Labs, Dartmouth, Nova Scotia

Table 18.

Tentative numbers of geochemical samples to be collected 1983 (based on 14 of 19 returned questionnaires)

Bedrock:	Sonic/RCD chips	≈150
	DDH core	≈2,500
	Grab	≈1,500
	Panels	≈500
Overburden:	Sonic/RCD	≈1,500
	Trenches/pits	1,000
Soils:		≈2,700 + ?
Streams:	Silts	≈50 + ?
	Panned Concentrates	?
	Waters	≈300

The correct interpretation of geochemical data requires that every available piece of information be brought to bear on the problem. One must have a thorough understanding of the fundamental principles of exploration geology of the area, trace element abundances in different rock types, primary dispersion, groundwater and surface water movement, climatic conditions, type of weathering, soil formation, glacial movement, type and distribution of vegetation and humus deposits, Eh and pH conditions, mobility of the elements, characteristics of the sampling medium (e.g. soils, sediments, waters), sampling methods employed and the analytical methods used to obtain the data. If one factor were to be singled out for special consideration, it would be the geology (in its broadest sense). A thorough knowledge of the geology would include such items as rock types, nature of weathering, soil formation, mineralization, structural geology and glacial history of an area; such information is the foundation for reliable interpretations. Regrettably, the geology of many areas in which exploration geochemistry is used is poorly known, and this adversely affects interpretations. If geophysical or other types of data are available, they should be incorporated in the interpretation process. Every effort should be made to use all available data from every source possible during the interpretation.

The analysis of exploration geochemical data has for the most part been empirical. Because of its essentially numeric character coupled with the lack as yet of well-defined mathematical models describing the source, migration and accumulation of minor and trace elements in rocks, it is not surprising that geochemical data have been subjected mainly to statistical analysis.

The use of statistics in exploration geochemistry, as in geology and geophysics, has increased significantly since the introduction of computers. However, it is essential that basic statistical principles be firmly fixed in the mind of the person utilizing geochemistry.

A) Basic Statistics - A Review

The ensuing review of basic statistics should not be considered as exhaustive. I am not a statistician. Rather, it should be regarded as a guide to the meaning and use of statistics to enhance the interpretation of data gathered during a geochemical survey.

It must be emphasized that in applying statistical functions to a set of data one assumes that the data are normally distributed. If this is not the case then the data must be normalized by either applying some form of transformation ($\log_{10}$ normalizing), by removing outliers (extremely high or low values clearly distinct from the main population) or by identification and separation of two or more populations (related to different rock types, soil horizons, variations in stream sediment composition, etc.). A first step in all of this is to examine the distribution of the data [redacted]. Histograms and/or frequency plots along with some basic statistical calculations can tell you a lot about your data:

Arithmetic Mean: ($\bar{x}$) of a set of n measurements x_1, x_2, $x_3 \ldots x_n$ is equal to the sum of measurements divided by n.

$$\bar{x} = \frac{x_1 + x_2 + x_3 \ldots\ldots x_n}{n}$$

Median: of a set of n measurements is defined as the value of the middle measurement (or average of two middle measurements) when the measurements are arranged in order of magnitude.

Mode: of a set of n measurements is that measurement that occurs with the greatest frequency.

For normal populations which have symmetrical frequency distributions the mean, mode and median coincide. For asymmetrical curves the mean > median > mode if skewed to the right and mode > median > mean if skewed to the left [redacted].

This gives us a start in statistically analyzing our data, but there are a number of other statistical functions that should be routinely examined in addition to mean, median and mode. These include minimum, maximum, range, standard deviation, skewness and kurtosis.

Range: of a set of n measurements x_1, $x_2, \ldots x_n$ is defined to be the difference between the maximum and minimum measurement.

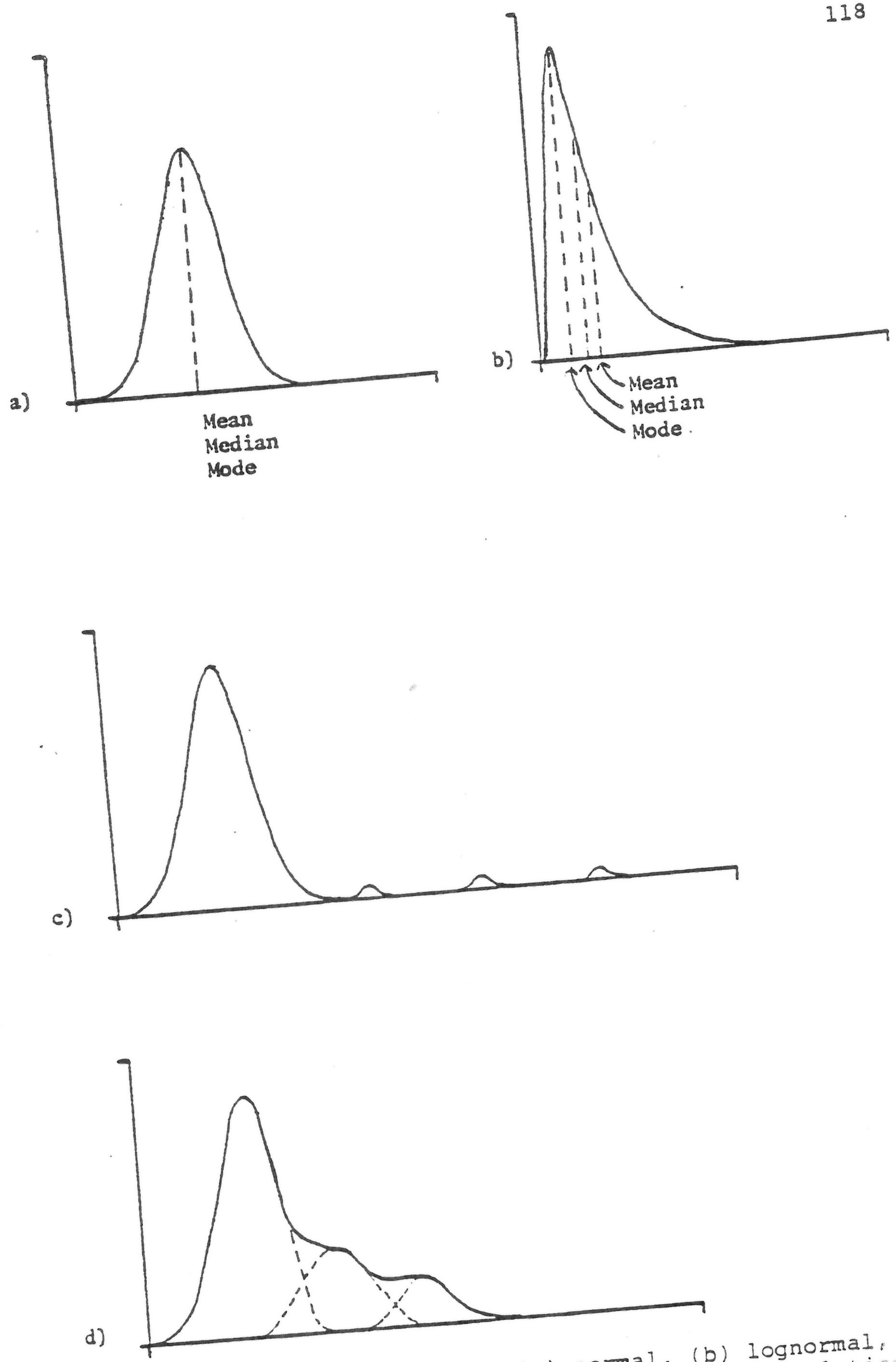


Figure 53. Frequency curves for (a) normal, (b) lognormal, (c) normal with outliers and (d) multipopulation distributions

Standard Deviation: of a set of n measurements x_1, x_2, $x_3, \ldots x_n$ is defined as equal to the positive square root of the square of the deviations of the measurements about their mean ($\bar{x}$).

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}}$$

Given a distribution of measurements that is approximately bell-shaped (i.e. normally distributed) the intervals ([redacted]:

a) ($\bar{x} \pm 1s$) will contain 68.27% of the measurements,

b) ($\bar{x} \pm 2s$) will contain approximately 95.45% of the measurements,

c) ($\bar{x} \pm 3s$) will contain approximately 99.73% of the measurements.

Kurtosis: is the degree of peakedness of a distribution, usually taken relative to a normal distribution ([redacted] It is normally measured by β_2 (beta two) or by α_4 (alpha 4) which have the same value expressed by the formula:

$$\beta_2 = \alpha_4 = \frac{M_4}{M_2^2} = \frac{\dfrac{\sum_{x_{i-n}} (x-\bar{x})^4}{n}}{\left(\sum_{x_{i-n}} \dfrac{(x-\bar{x})^2}{n}\right)^2}$$

M = moment about the mean (M_4 = fourth, M_2 = second)

The greater the value of β_2, the more peaked the distribution. A normal distribution has a β_2 of 3 (Figure 55).

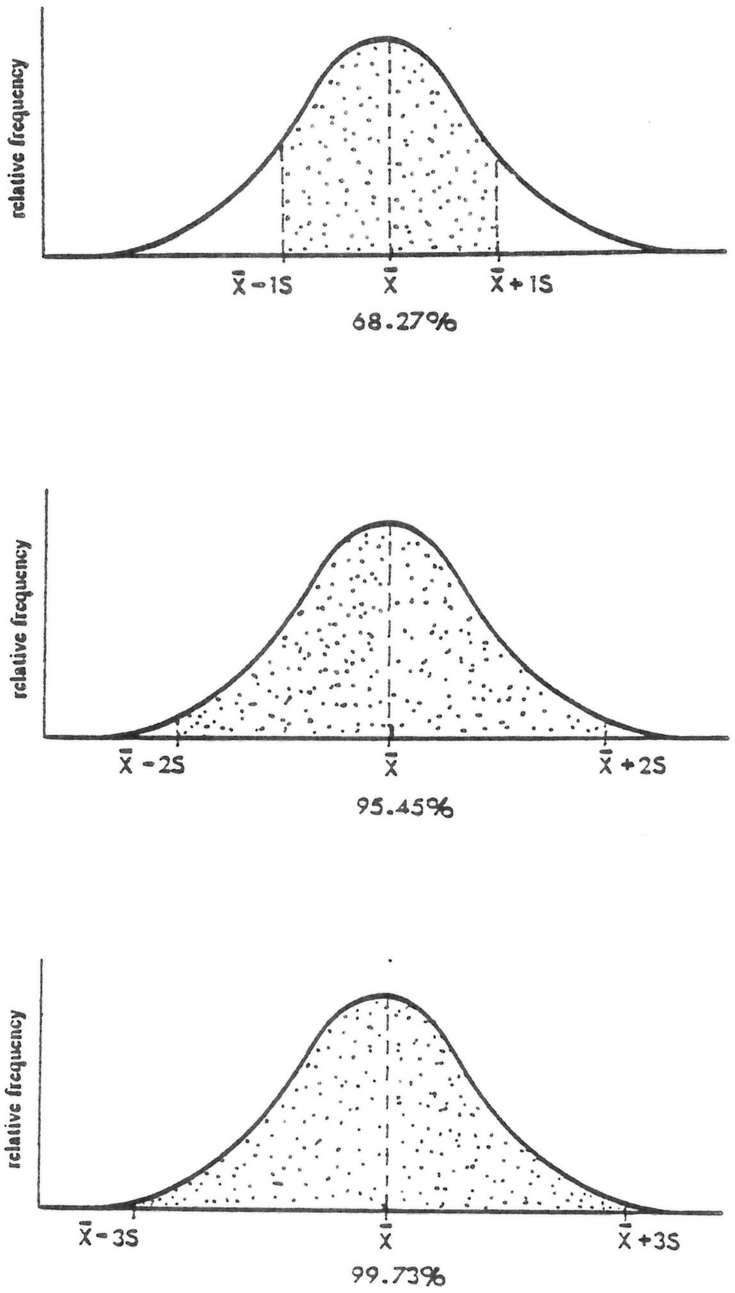


Figure 54. Distribution of ($\bar{x}$ ± 1s), ($\bar{x}$ ± 2s) and ($\bar{x}$ ± 3s) data for a normal population

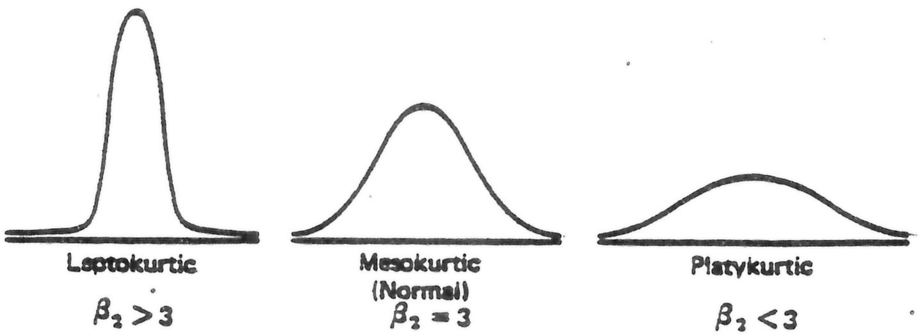


Figure 55. Kurtosis nomenclature for peaked, flat and normal (bell-shaped) data distribution

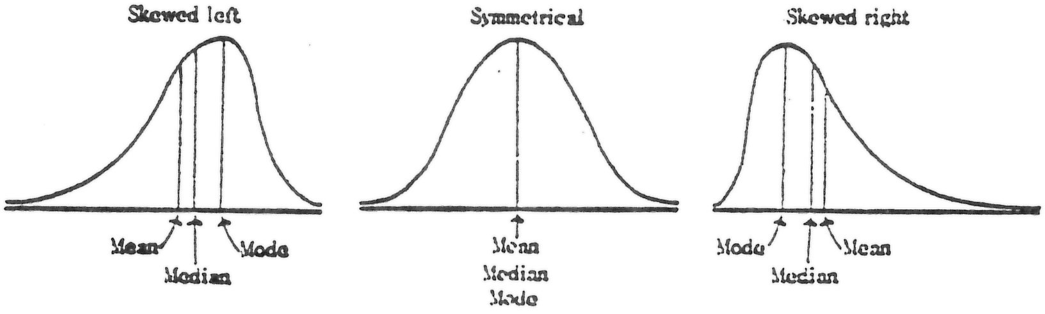


Figure 56. Relationship of mean, median and mode as determined by direction of skewness

Skewness: is the degree of asymmetry or departure from symmetry of a distribution [redacted] If it is a normal (bell-shaped) curve, skewness equals 0. If the curve is skewed to the right (i.e. the mean lies to the right of the median and mode), skewness is positive; to the left, negative. This function basically tells us about the distribution of our data, and whether or not we are dealing with a normal population.

Skewness can be calculated using Pearson's second coefficient of skewness:

$$\text{Skewness} = \frac{3\ (\bar{x} - \text{median})}{s} = \frac{3\ (\text{mean} - \text{median})}{\text{standard deviation}}$$

If we are dealing with a simple population of relatively normally distributed data then we can use ($\bar{x}$ + 2s) as our threshold value in our intitial interpretation of the data.

In the case where the data proves to be log-normal [redacted] the data must first be $\log_{10}$ transformed before computation of the geometric mean and standard deviation.

Geometric Mean: ($\bar{y}$) of a set of n measurements x_1, x_2, $x_3, \ldots x_n$ is equal to the n^th^ root of the product of the numbers.

$$\bar{y} = \sqrt[n]{x_1\ x_2\ x_3 \ldots\ldots x_n}$$

If the median and geometric mean are in agreement, the distribution is likely log-normal whereas if the median and arithmetic mean are in agreement, the distribution is probably normal.

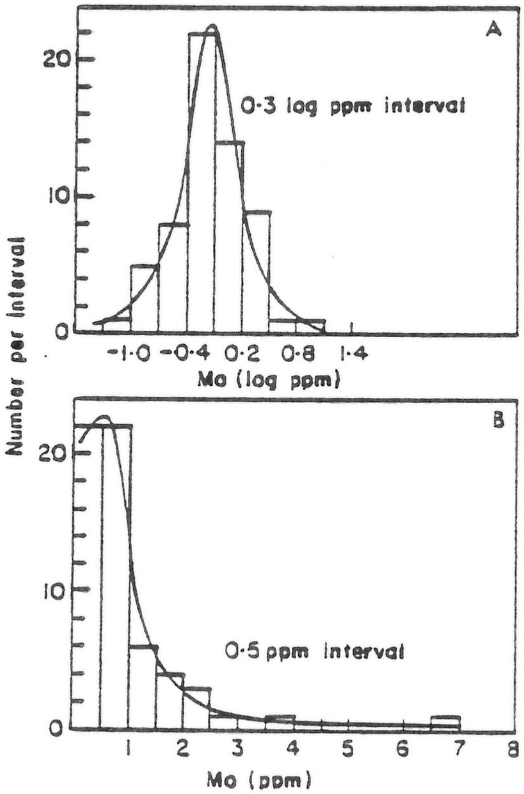


Figure 57. Log$_{10}$ transformed (a) vs untransformed (b) Mo data from a granite body

If the data are log-normal, the geometric mean and geometric standard deviation can be used to determine threshold levels for initial interpretation.

Other forms of transformation exist, but most geochemical data are either normally or log-normally distributed.

Where outliers exist in the data, these must be removed before statistical analysis. Sometimes $\log_{10}$ transformation of the data can rectify this problem, but if the outlier(s) are too extreme even this will not help.

In the instance where a data set is composed of more than one population, these must be separated before statistical analyses. It may be a simple problem to identify and sort them (i.e. based on rock type or soil horizon). It may also be a very complex relationship so that the populations are not easily sorted. The use of cumulative frequency plots and/or probability plots can be used to disect multipopulation data sets [redacted]. The cumulative percent scale on probability paper is graduated so that a normal distribution plots as a straight line. A mixture of two normal populations plots as nearly linear segments separated by curved segments containing an inflection point. Log-normal distributions plot as a straight line if a log scale is used for concentration or if the data are log-transformed before being plotted on an arithmetic scale. The result for a combination of two log-normal populations is an s-shaped curve. The inflection

Gardin
data
Naftali

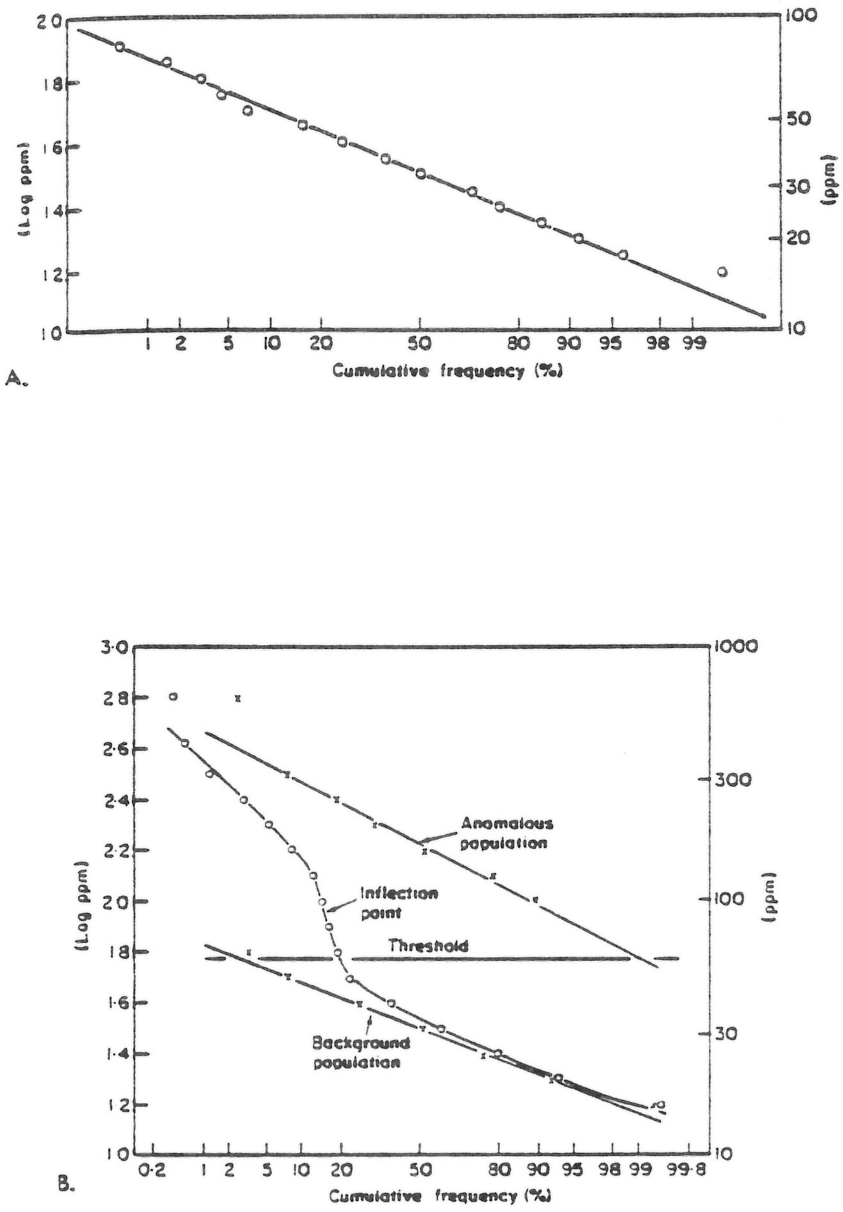


Figure 58. Log probability plot of a single background population (a) and of two combined populations (b)

point gives an estimate of the proportions of the two populations in the mixture; for instance, proportions of 16% and 84% are indicated from the inflection point shown on Figure 58b. The curve may then be partitioned into two curves and threshold values for each population determined. The use of probability plots is a somewhat complex procedure.

So far, we have only been discussing univariate statistics, those that apply to one variable at a time. There is a whole range of bivariate statistics including ratioing, correlation analysis, regression analysis (simple linear and multiple linear), factor analysis and cluster analysis which are commonly used to evaluate geochemical data. Before we can apply these more sophisticated data interpretational methods, we need to first evaluate our data using simple statistics. Much of our geochemical data needs to be computerized before anything else can be done to it. I will defer any further discussion on bivariate statistics to another session at a later date.

B) Geochemical Data Management

Geochemical data interpretation carried out to date within Kidd has generally, but not exclusively, been superficial due to time constraints and, most significantly, due to the form in which geochemical data are currently handled. The lack of any appreciable co-ordinated computerized geochemical data entry, documentation, statistical analyses and archival system of data management within Kidd, with the exception of the Whole Rock Data Base, is probably the single largest deterrent preventing either basic or sophisticated data interpretations.

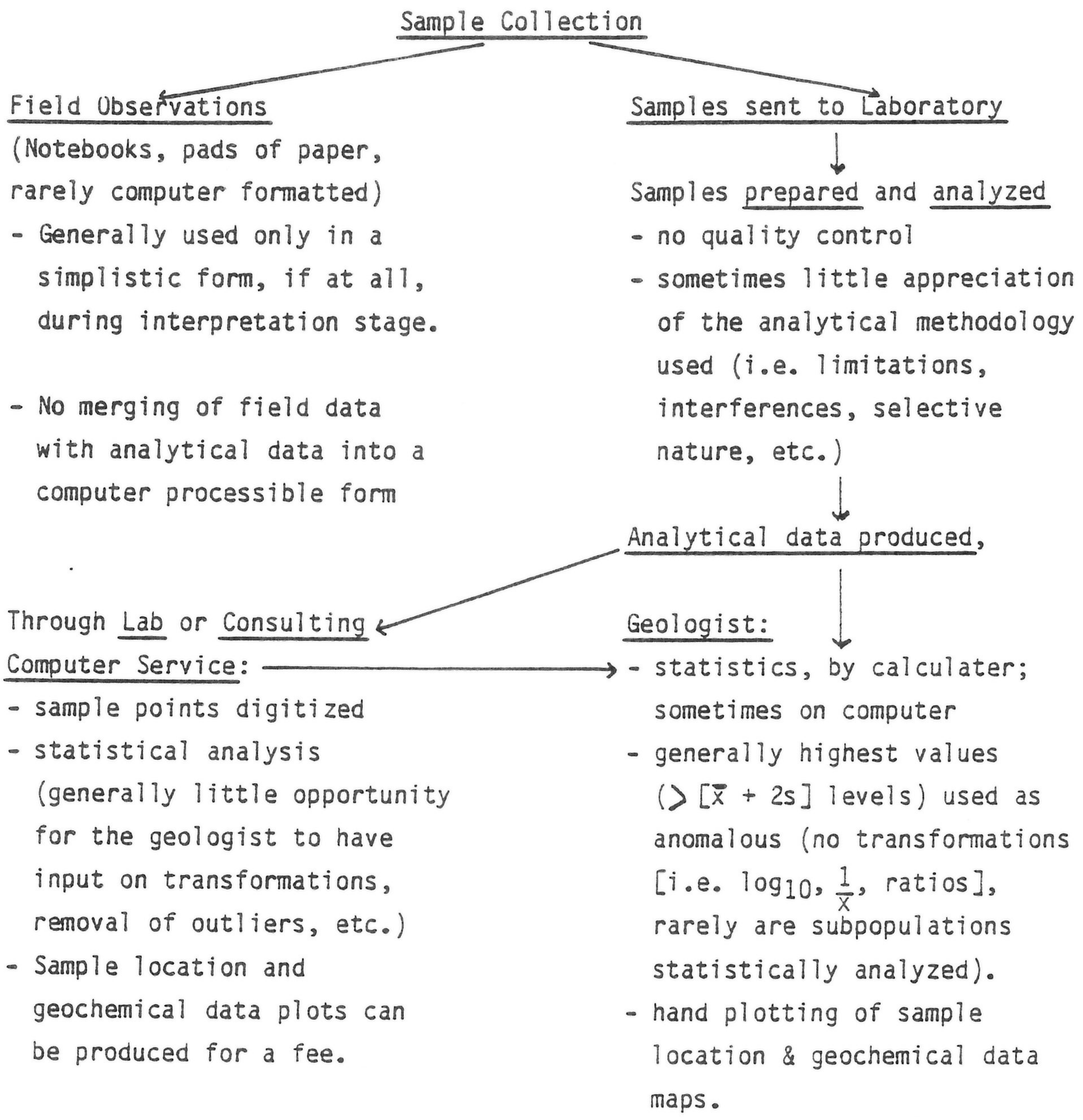
The current system of geochemical exploration within Kidd Creek Mines Ltd., as I see it, is summarized in Figure 59.

This system gives no documentation/archiving of field techniques, field observations or of the analytical methods employed. Sometimes this information is given in the project reports but generally not in any detail. There is little information available on the specifics of the above except in the mind or notes of the project geologist. In time, and most certainly if a geologist leaves, much of the information is lost, and any attempt to re-interpret the data is difficult if not impossible.

We are currently in the planning stages of setting up an effective but flexible data management system (Figure 60). Field information must be coded on field cards and merged with systematically formatted analytical data into files with adequate documentation (i.e. sampling methodologies, sample types, preparation, analytical techniques, etc.). This will enable simple statistical analyses of the combined field and analytical data to be performed, and with relative ease, more sophisticated interpretational techniques can also be employed.

A number of computer programs to manipulate, plot, statistically analyze and produce data reports are currently

Figure 59. Current (1982) Geochemical Exploration Methodology
Kidd Creek Mines Ltd.



Sample Collection

Field Observations
(Notebooks, pads of paper, rarely computer formatted)
- Generally used only in a simplistic form, if at all, during interpretation stage.
- No merging of field data with analytical data into a computer processible form

Samples sent to Laboratory

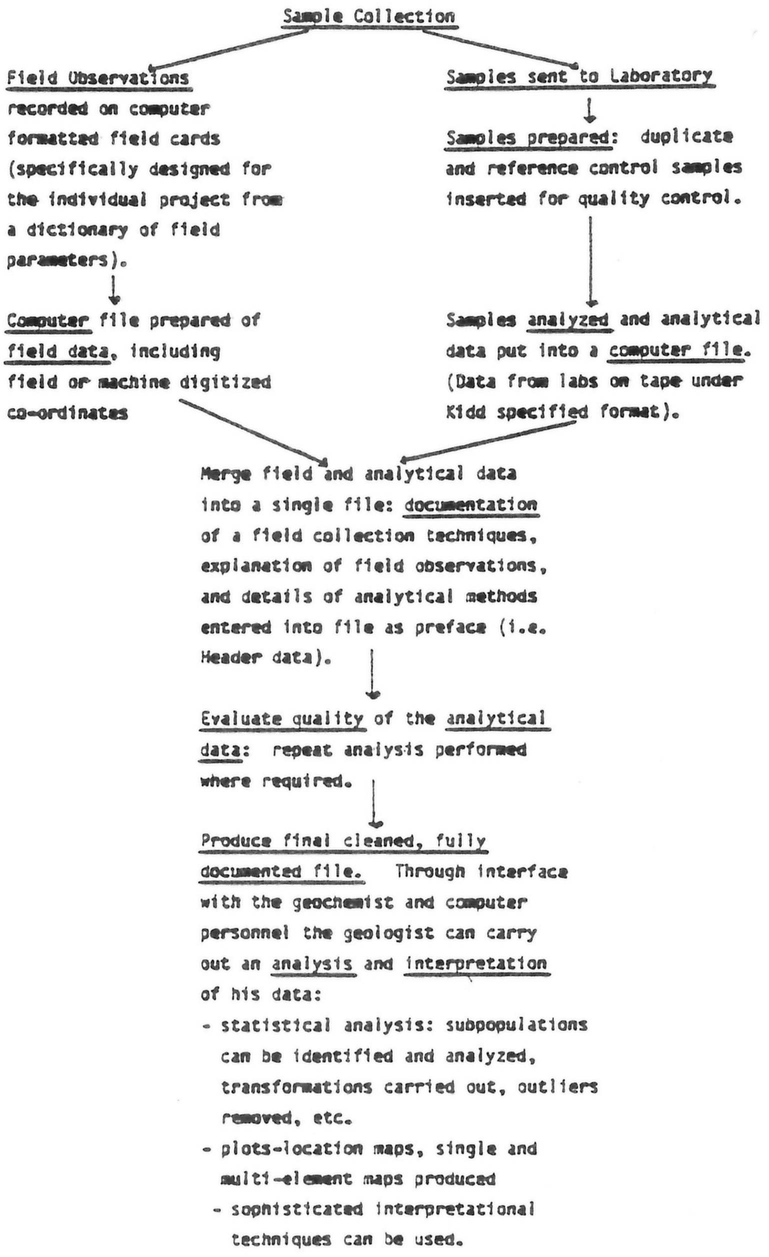
Samples prepared and analyzed
- no quality control
- sometimes little appreciation of the analytical methodology used (i.e. limitations, interferences, selective nature, etc.)

Analytical data produced,

Through Lab or Consulting Computer Service:
- sample points digitized
- statistical analysis (generally little opportunity for the geologist to have input on transformations, removal of outliers, etc.)
- Sample location and geochemical data plots can be produced for a fee.

Geologist:
- statistics, by calculater; sometimes on computer
- generally highest values ($> [\bar{x} + 2s]$ levels) used as anomalous (no transformations [i.e. $\log_{10}$, $\frac{1}{x}$, ratios], rarely are subpopulations statistically analyzed).
- hand plotting of sample location & geochemical data maps.

Figure 60. Proposed Geochemical Exploration Methodology - Kidd Creek Mines Ltd.



Sample Collection

Field Observations recorded on computer formatted field cards (specifically designed for the individual project from a dictionary of field parameters).

Computer file prepared of field data, including field or machine digitized co-ordinates

Samples sent to Laboratory

Samples prepared: duplicate and reference control samples inserted for quality control.

Samples analyzed and analytical data put into a computer file. (Data from labs on tape under Kidd specified format).

Merge field and analytical data into a single file: documentation of a field collection techniques, explanation of field observations, and details of analytical methods entered into file as preface (i.e. Header data).

Evaluate quality of the analytical data: repeat analysis performed where required.

Produce final cleaned, fully documented file. Through interface with the geochemist and computer personnel the geologist can carry out an analysis and interpretation of his data:

- statistical analysis: subpopulations can be identified and analyzed, transformations carried out, outliers removed, etc.
- plots-location maps, single and multi-element maps produced
- sophisticated interpretational techniques can be used.

available through the Exploration Division's computer facility in Timmins. Of these, the Whole Rock Data Base (WRDB) programs are the furthest along in development. The WRDB stores descriptive and analytical data about a rock sample ([redacted]. Both of these kinds of data can be manipulated and retrieved, through user-friendly interactive programs, and used for reports ([redacted], plots ([redacted] and maps. A number of other programs for handling geochemical data are also available:

1. Basic Statistics (Figure 67)
2. Histogram Plots (Figure 68)
3. Cumulative Frequency (Figure 69)
4. Ternary Plots (Figure 70)
5. Scatter Diagrams (X-Y Plots) (Figure 71)
6. Map Plots
7. Contour Plots

Unfortunately, these programs are not interactive user-friendly and require that specific instructions from the geologist regarding his data be detailed to the people running them. Work is in progress to develop an interactive user-friendly basic statistics-histogram-cumulative frequency program (Figures 72 and 73). This program will be for use with the WRDB and all other geochemical data files (Overburden, Soil/Overburden, Stream) now under development. Some work has also been done on an interactive program for dissecting multipopulation geochemical data using cumulative frequency plots. Development work towards achieving geochemical maps which routinely include the histograms, cumulative frequency plots

FLOW SHEET OF THE DATA BASE AS THE USER SEES IT

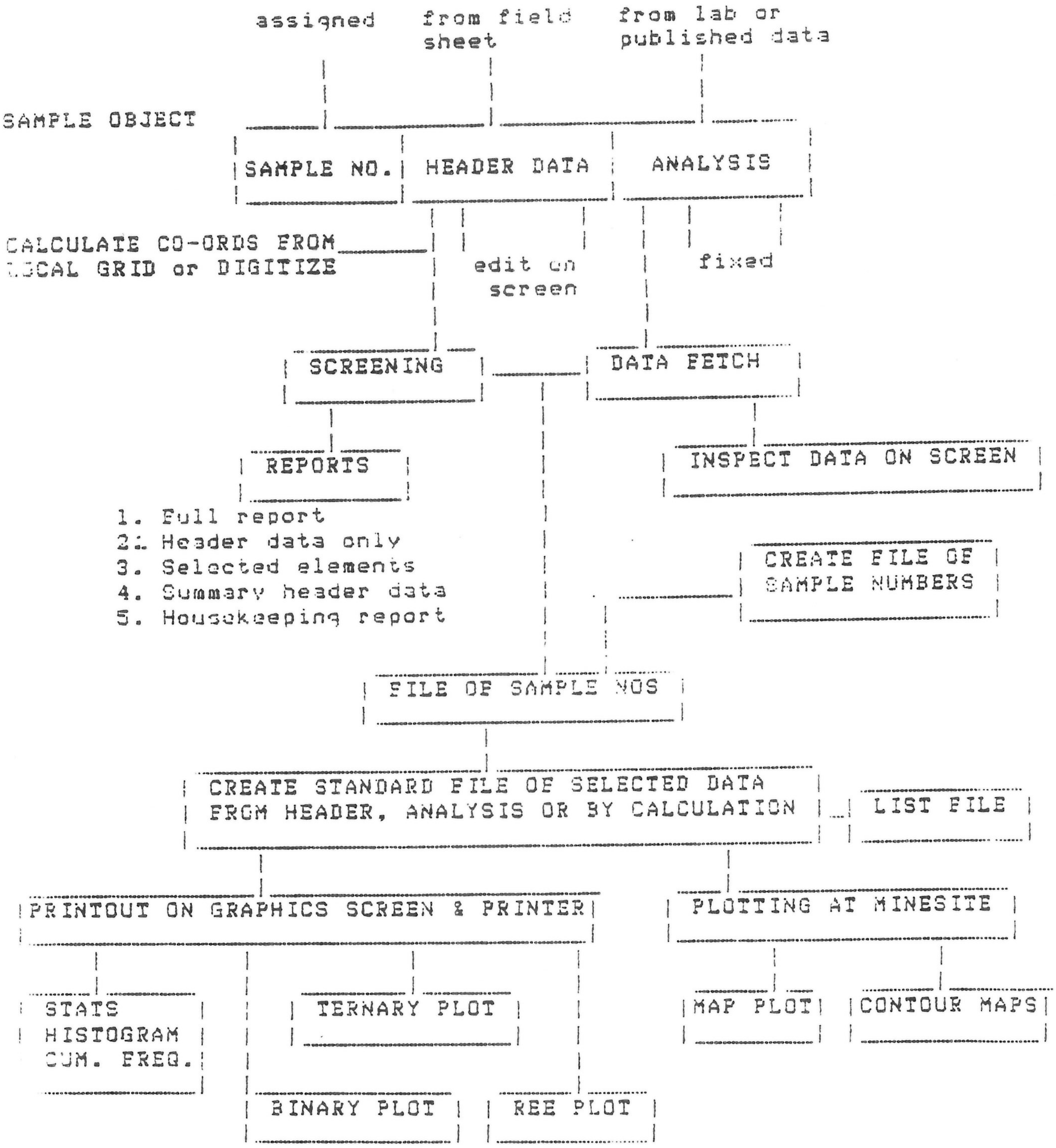


Figure 61. Whole Rock Data Base Flow Diagram

```
                         KIDD CREEK MINES - WHOLE ROCK DATABASE

                               NORTH OF PROSSER COMPILATION
                               ----------------------------
                                                                    Rock Description
Sample    Field      Proj                                               Field Name                   Sampled by
  No.       No.      Code   Prov  NTS     Township      ---------------------------------------   -------------
-------  -----------  ------ ----  ------  -----------

AA12865 FRP-82-1     ABCOM  ONT   42A14   REAUME         PLUTONIC.ULTRAMAFIC.MEDIUM.              FRANK PLOEGER
                                                         MASSIVE.EQUIGRANULAR.
                                                         PERVASIVE.SERPENTINE.STRONG.
                                                         NIL.NIL.NO COMMENT.

AA12866 FRP-82-2     ABCOM  ONT   42A14   REAUME         PLUTONIC.ULTRAMAFIC.MEDIUM.              FRANK PLOEGER
                                                         MASSIVE.EQUIGRANULAR.
                                                         PERVASIVE.SERPENTINE.STRONG.
                                                         DISSEMINATED AND BLEBS.< 1%.PYRITE.

AA12867 FRP-82-3     ABCOM  ONT   42A14   REAUME         PLUTONIC.ULTRAMAFIC.MEDIUM.              FRANK PLOEGER
                                                         MASSIVE.EQUIGRANULAR.
                                                         PERVASIVE.SERPENTINE.WEAK.
                                                         NIL.NIL.

AA12868 FRP-82-4     ABCOM  ONT           REAUME         PLUTONIC.MAFIC.COARSE.                   FRANK PLOEGER
                                                         MASSIVE.
                                                         PERVASIVE.CHLORITIZATION.MODERATE.
                                                         DISSEMINATED AND BLEBS.< 1%.
                                                         PYRRHOTITE.

AA12869 FRP-82-5     ABCOM  ONT   42A14   REAUME         PLUTONIC.MAFIC.MEDIUM.                   FRANK PLOEGER
                                                         MASSIVE.
                                                         PERVASIVE.CHLORITIZATION.MODERATE.

AA12870 FRP-82-6     ABCOM  ONT   42A14   REAUME                                                  FRANK PLOEGER

                                                         PERVASIVE.CHLORITIZATION.MODERATE.
                                                         DISSEMINATED AND BLEBS.< 1%.
                                                         PYRRHOTITE PLUS CHALCOPYRITE.

AA12871 FRP-82-7     ABCOM  ONT   42A14   REAUME         PLUTONIC.MAFIC.COARSE.                   FRANK PLOEGER
                                                         MASSIVE.
                                                         PERVASIVE.CHLORITIZATION.MODERATE.
                                                         NIL.NIL.
```

Figure 62. Example of a WRDB header data summary report produced from a menu by the user

```
                  KIDD CREEK MINES-WHOLE ROCK DATABASE

          EXAMPLE OF ANALYTICAL REPORT RP2002 OUTPUT FOR ABITIBI AREA
          ===========================================================

SAMP NO.->   AA10001   AA10002   AA10216   AA10217   TA02419   TA02420
---------------------------------------------------------------------
SIO2           48.43     50.73      0.00      0.00     48.39     49.51
AL2O3          15.62     15.44      0.00      0.00     15.01     13.91
FE2O3          13.12     15.26      0.00      0.00     13.27     13.96
MNO             0.19      0.19      0.00      0.00      0.17      0.21
MGO             6.23      3.10      0.00      0.00      5.48      5.47
CAO            10.49      8.62      0.00      0.00      6.94      8.96
NA2O            2.01      2.45      0.00      0.00      1.99      2.65
K2O             0.54      1.02      0.00      0.00      0.20      1.20
TIO2            0.87      1.65      0.00      0.00      1.22      1.06
P2O5            0.09      0.25      0.00      0.00      0.11      0.12
CR2O3          -0.01     -0.01      0.00      0.00      0.00      0.00
LOI             0.70      1.08      0.00      0.00      7.54      2.00
             -------   -------   -------   -------   -------   -------
TOTAL          98.28     99.78      0.00      0.00    100.32     99.05

AU              6.00     -1.00      0.00      0.00      0.00      0.00
AG             -0.50     -0.50      0.00      0.00      0.00      0.00
CU            250.00    190.00      0.00      0.00      0.00      0.00
NI             96.00     30.00      0.00      0.00      0.00      0.00
PB              8.00     10.00      0.00      0.00      0.00      0.00
ZN            130.00    180.00      0.00      0.00     70.00    150.00
SR            130.00    150.00      0.00      0.00    -10.00     20.00
RB             10.00     20.00      0.00      0.00
```

Figure 63. Example of an analytical data report produced from WRDB data

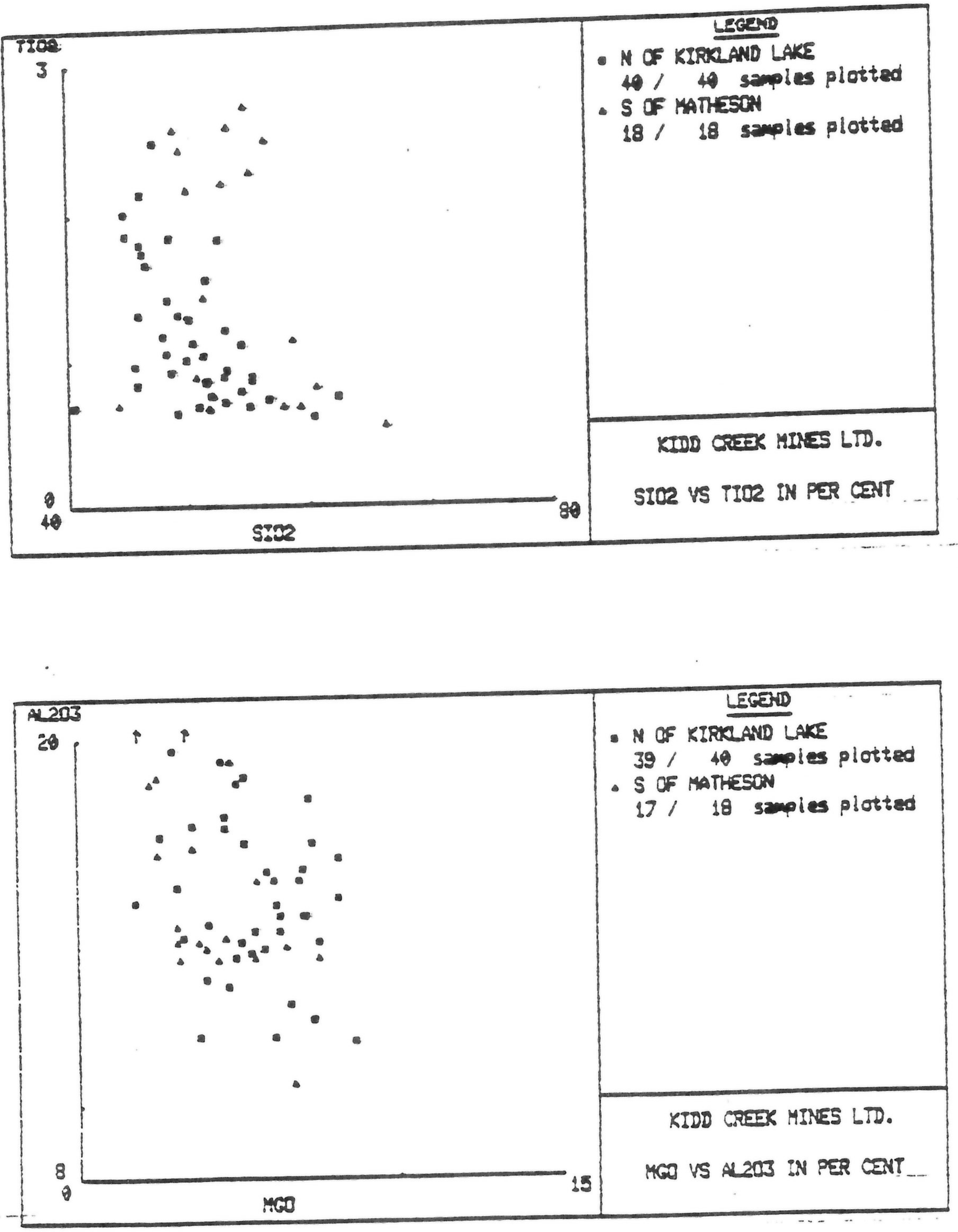
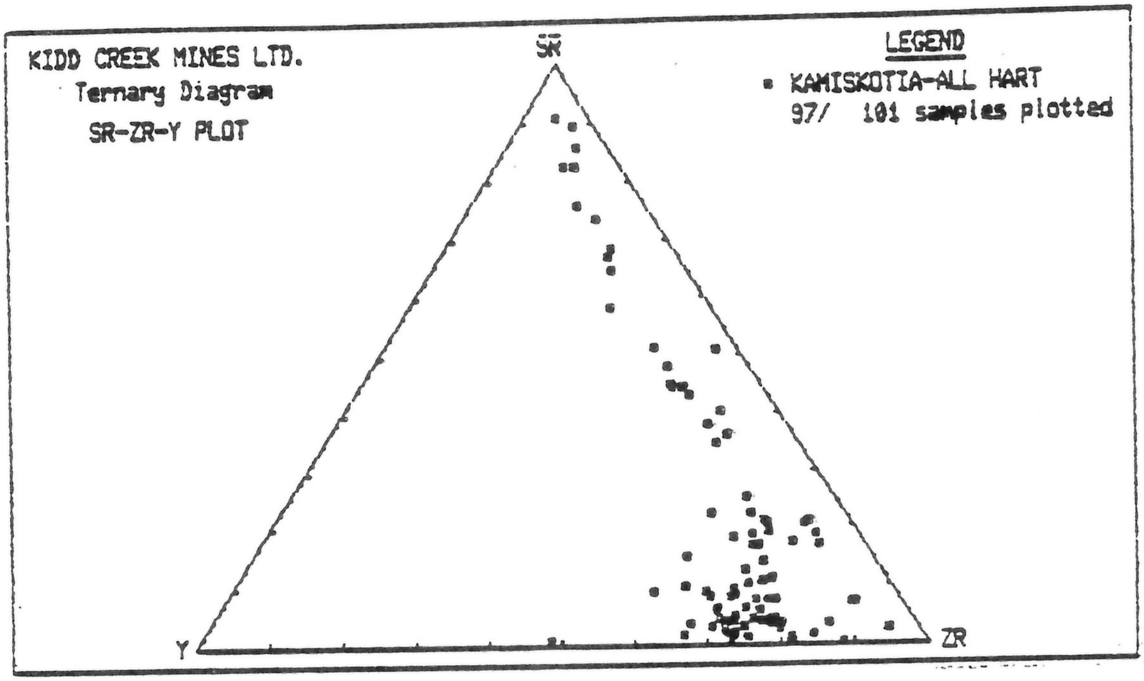


Figure 64. Example of a binary plot produced on a printer using WRDB data



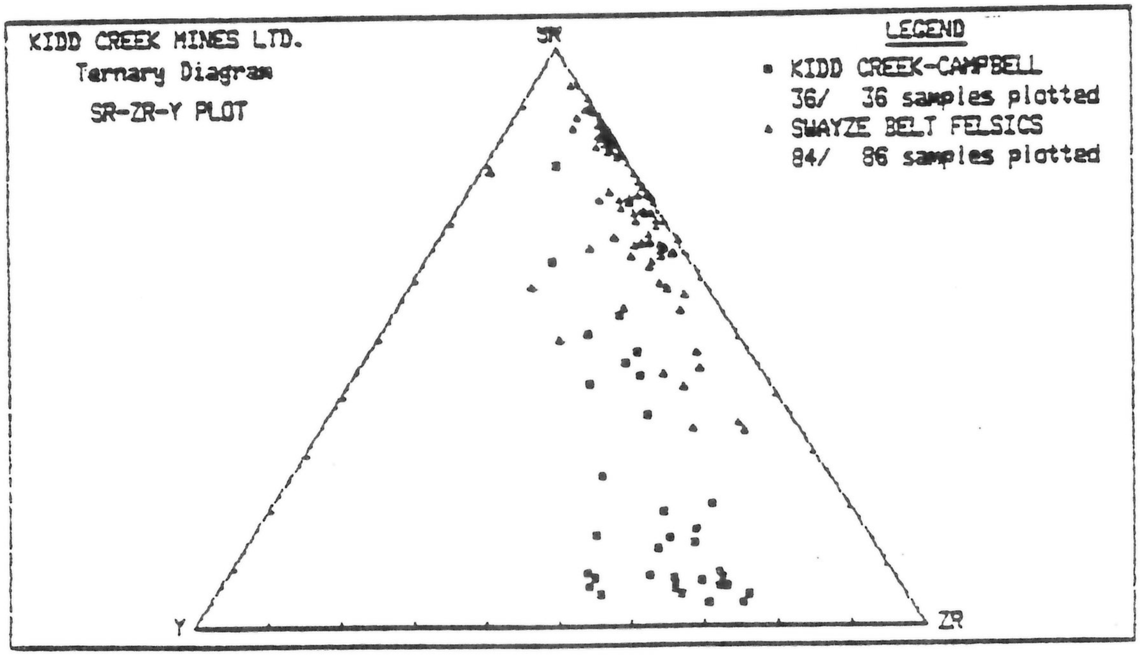


Figure 65. Example of a ternary diagram plot produced on a printer using WRDB data

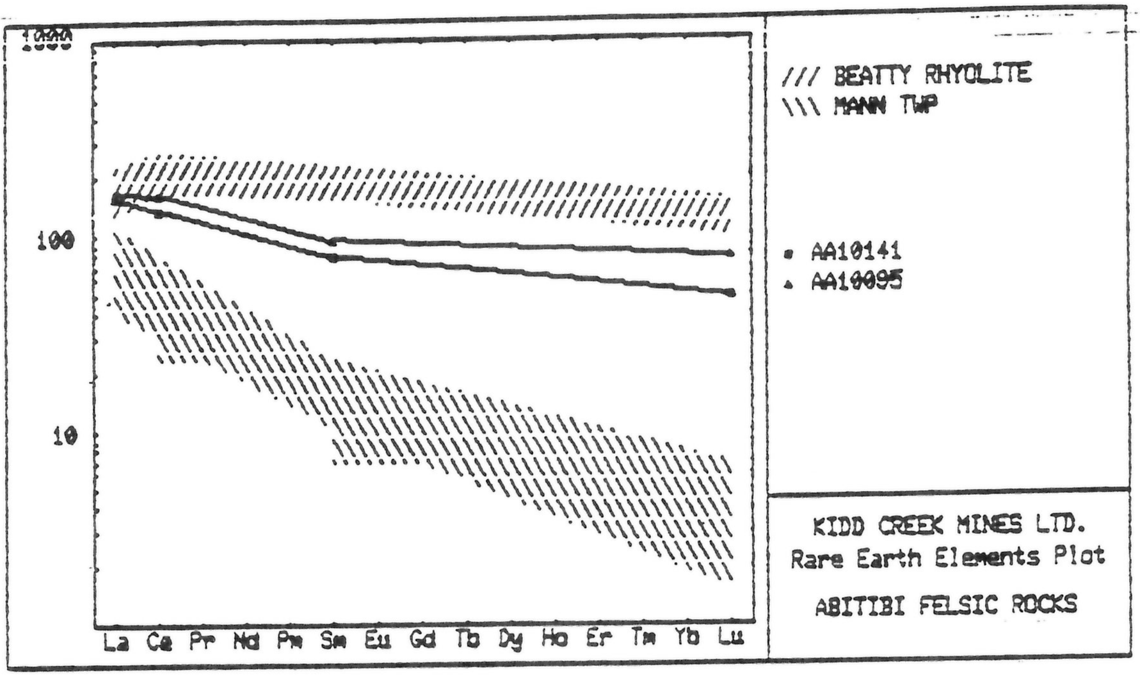


Figure 66. Example of a REE plot produced on a printer using WRDB data

```
MOOSE GRID
PROJ.#04   PB (PPM) IN SOILS
RAW DATA

        ** STATISTICS **

        TOTAL NUMBER OF SAMPLES                               248
        NUMBER OF "TRACE" SAMPLES                               0
        NUMBER OF "NON DETECTABLE" SAMPLES                      0

        MINIMUM VALUE                                      2.0000
        MAXIMUM VALUE                                   1160.0000
        MEAN                                              44.6492
        STANDARD DEVIATION                               112.5498
        VARIANCE                                       12667.1600
        MEDIAN                                            11.0000
        MODE                                               6.0000
        SKEWNESS                                           6.8416
        KURTOSIS                                          75.2419
        CLASS INTERVAL                                    69.0000
        NUMBER OF CLASSES                                      20

        * PERCENTILES *

        MINIMUM VALUE                                      2.0000
        25TH PERCENTILE <1ST QUARTILE>                     8.0000
        50TH PERCENTILE <MEDIAN>                          11.0000
        75TH PERCENTILE <3RD QUARTILE>                    16.0000
        80TH PERCENTILE                                   40.0000
        90TH PERCENTILE                                   81.0000
        95TH PERCENTILE                                  227.0000
        98TH PERCENTILE                                  391.0000
        99TH PERCENTILE                                  420.0000
        MAXIMUM VALUE                                   1160.0000

        * MOMENTS *

        FIRST MOMENT <MEAN>                               44.6492
        SECOND MOMENT                                  14661.0117
        THIRD MOMENT                                12400526.0000
        FOURTH MOMENT                            ****************
        FIFTH MOMENT                             ****************

        FIRST MOMENT ABOUT THE MEAN                       -0.0001
        SECOND MOMENT ABOUT THE MEAN <VARIANCE>        12667.4679
        THIRD MOMENT ABOUT THE MEAN                 10120739.0000
        FOURTH MOMENT ABOUT THE MEAN             ****************
        FIFTH MOMENT ABOUT THE MEAN              ****************
```

```
MOOSE GRID
PROJ.#04   PB (PPM) IN SOILS
TRUNCATED LOG DATA

        ** STATISTICS **

        TOTAL NUMBER OF SAMPLES                               247
        NUMBER OF "TRACE" SAMPLES                               0
        NUMBER OF "NON DETECTABLE" SAMPLES                      0

        MINIMUM VALUE                                      0.3010
        MAXIMUM VALUE                                      2.6532
        MEAN                                               1.2378
        STANDARD DEVIATION                                 0.4640
        VARIANCE                                           0.2141
        MEDIAN                                             1.1139
        MODE                                               0.7782
        SKEWNESS                                           0.7677
        KURTOSIS                                           0.6127
        CLASS INTERVAL                                     0.1176
        NUMBER OF CLASSES                                      20

        * PERCENTILES *

        MINIMUM VALUE                                      0.3010
        25TH PERCENTILE <1ST QUARTILE>                     0.9031
        50TH PERCENTILE <MEDIAN>                           1.1139
        75TH PERCENTILE <3RD QUARTILE>                     1.4771
        80TH PERCENTILE                                    1.5911
        90TH PERCENTILE                                    1.9031
        95TH PERCENTILE                                    2.3222
        98TH PERCENTILE                                    2.5775
        99TH PERCENTILE                                    2.5999
        MAXIMUM VALUE                                      2.6532

        * MOMENTS *

        FIRST MOMENT <MEAN>                                1.2378
        SECOND MOMENT                                      1.7465
        THIRD MOMENT                                       2.8774
        FOURTH MOMENT                                      5.2484
        FIFTH MOMENT                                      11.4067

        FIRST MOMENT ABOUT THE MEAN                        0.0000
        SECOND MOMENT ABOUT THE MEAN <VARIANCE>            0.2141
        THIRD MOMENT ABOUT THE MEAN                        0.1104
        FOURTH MOMENT ABOUT THE MEAN                       0.1963
        FIFTH MOMENT ABOUT THE MEAN                        0.1942
```

Figure 67. An example of output from the basic statistics program

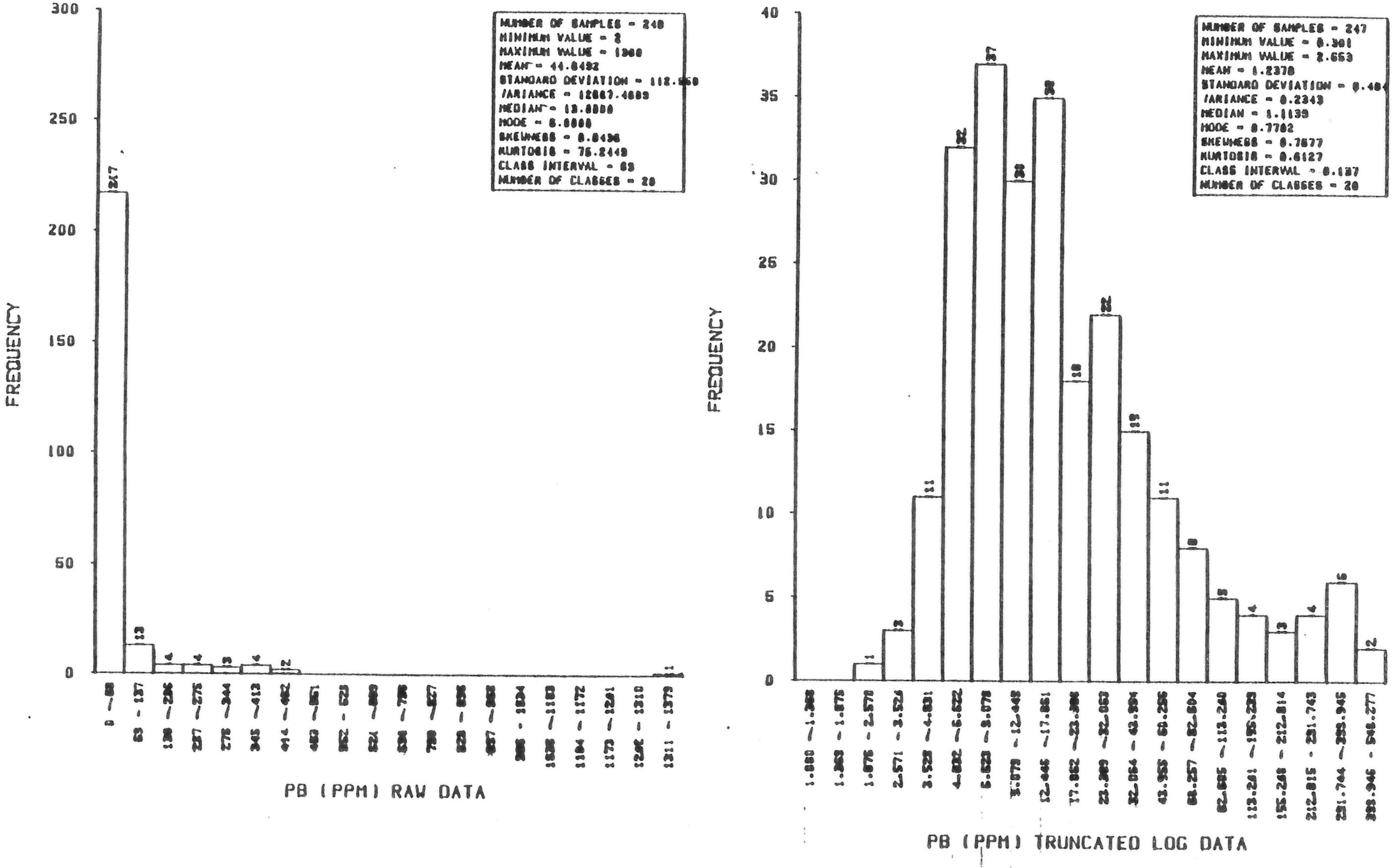


FIGURE : MOOSE GRID
PROJ.#04 PB (PPM) IN SOILS

FIGURE : MOOSE GRID
PROJ.#04 PB (PPM) IN SOILS

Figure 68. An example of a histogram plot

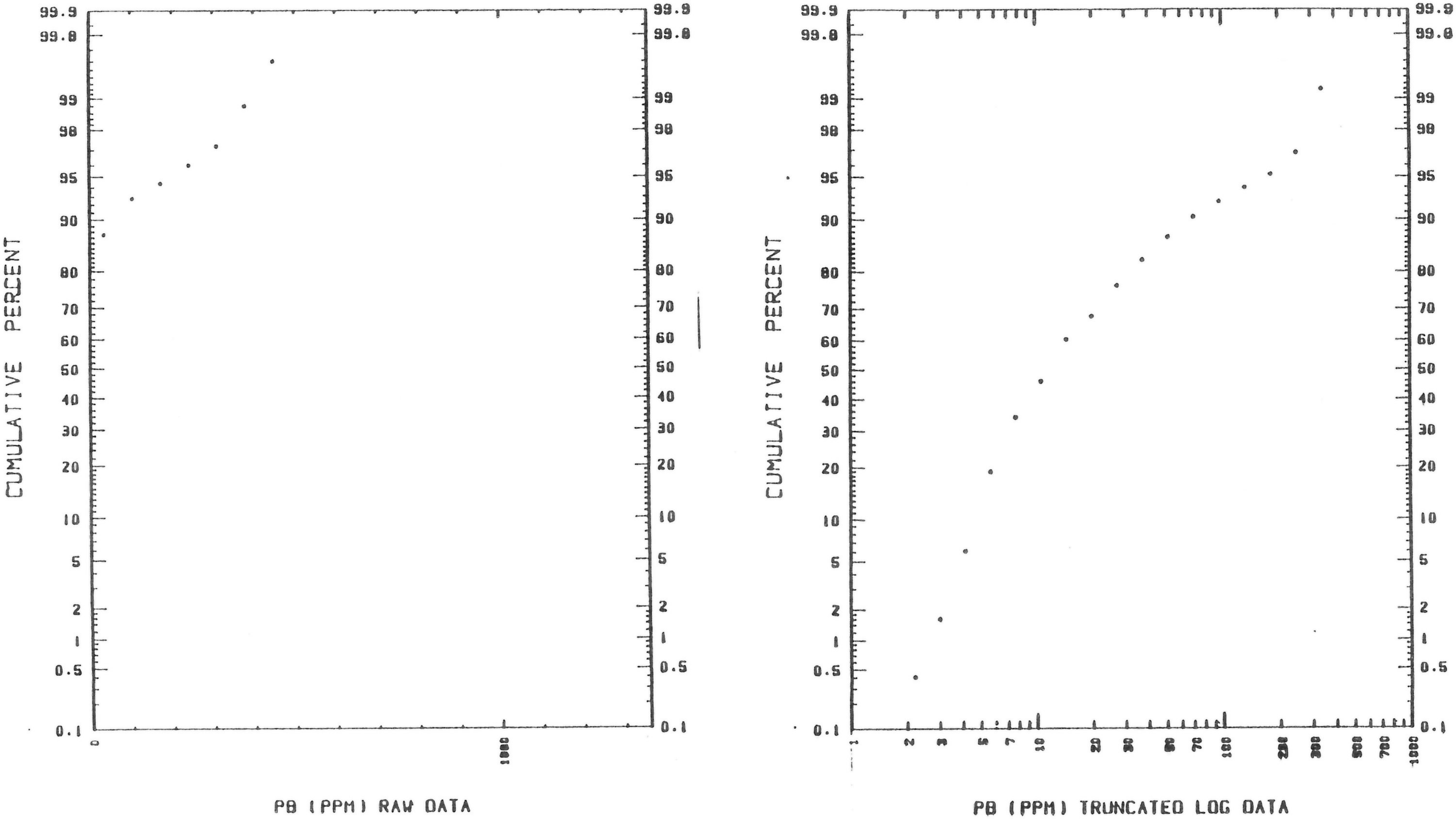


FIGURE : MOOSE GRID
PROJ.#04 PB (PPM) IN SOILS

FIGURE : MOOSE GRID
PROJ.#04 PB (PPM) IN SOILS

Figure 69. An example of a cumulative frequency plot

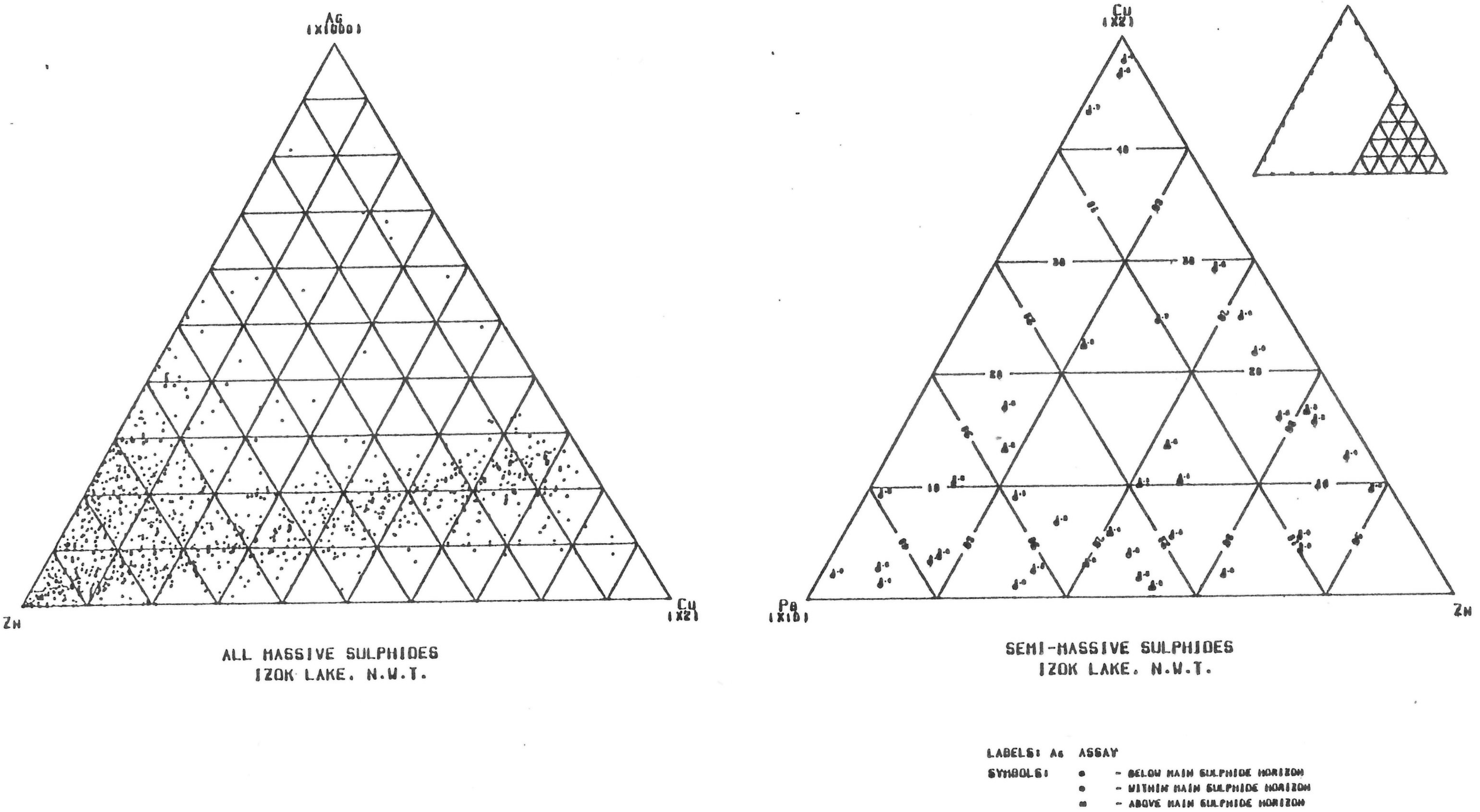


Figure 70. An example of a ternary plot

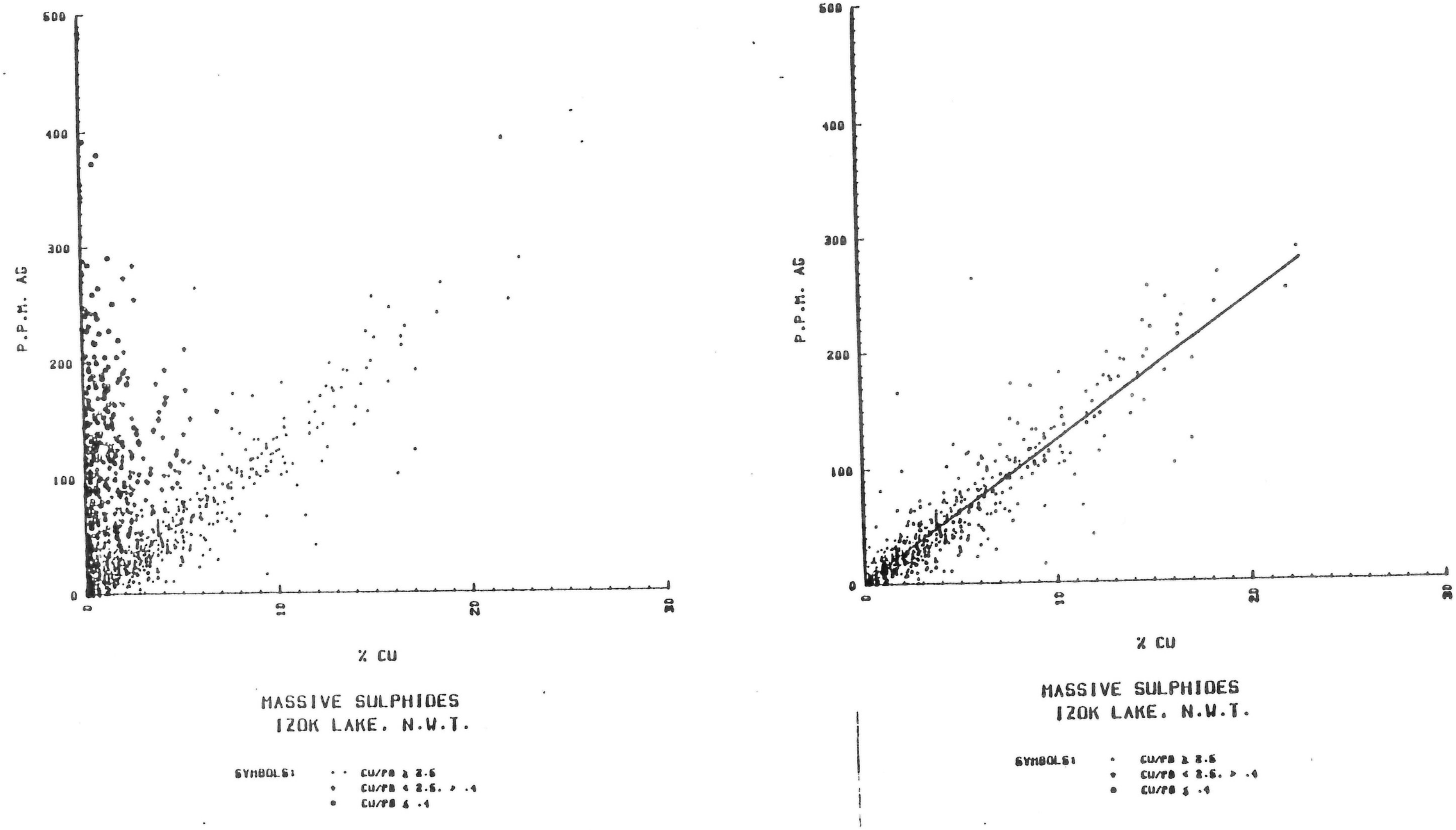


Figure 71. An example of a scatter diagram (X-Y) plot

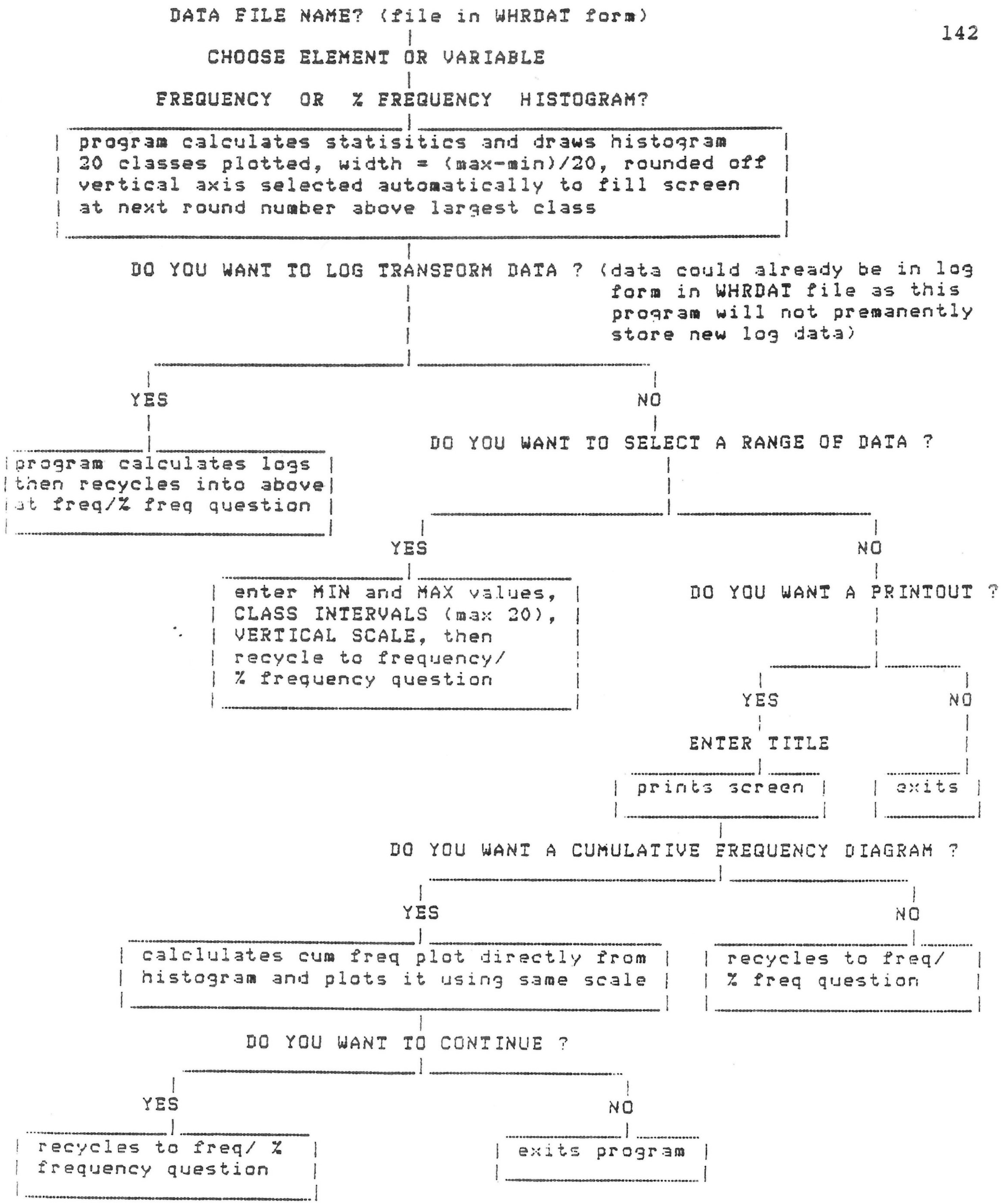
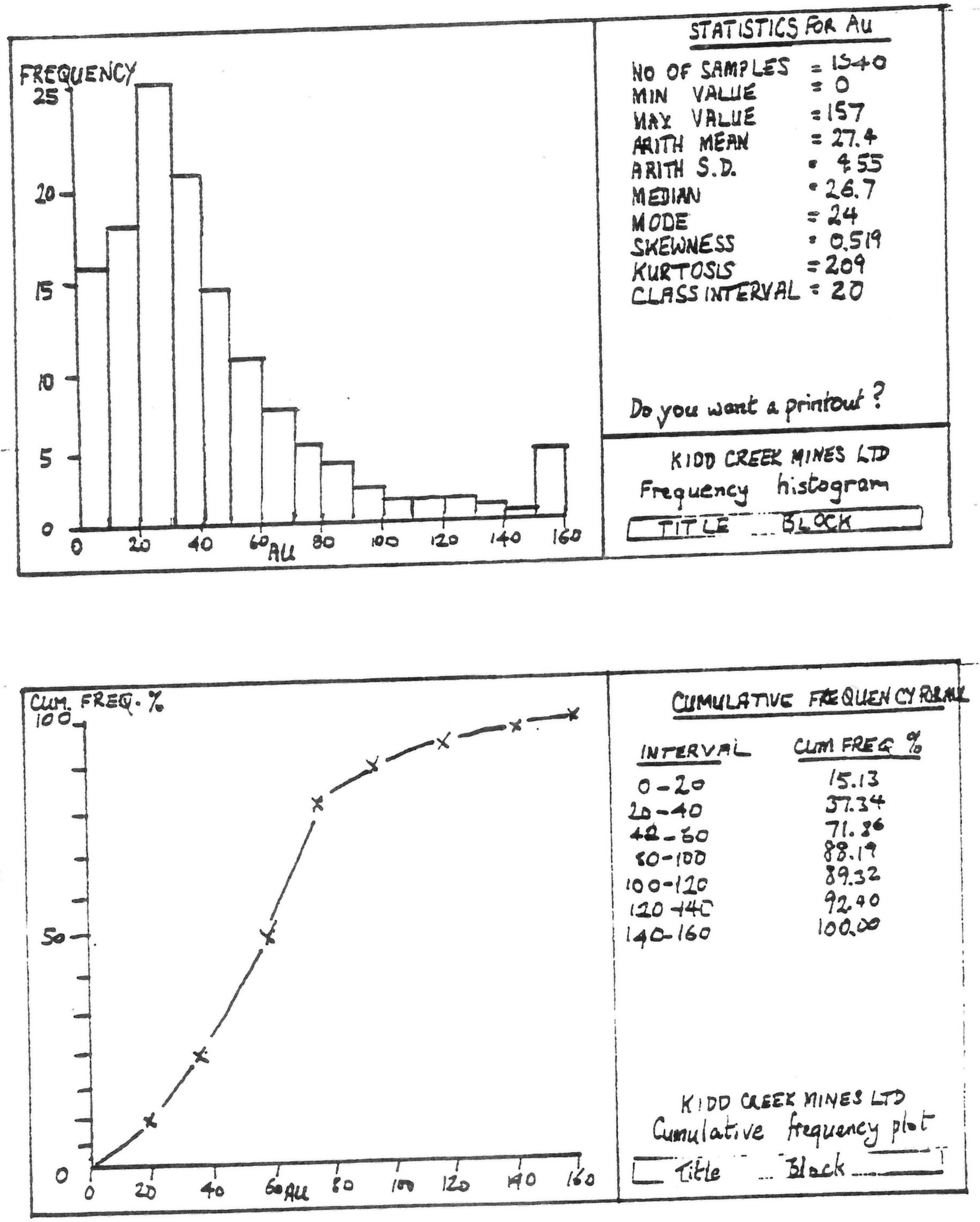


Figure 72. Proposed interactive statistics-histogram-cumulative frequency program



STATISTICS FOR AU

NO OF SAMPLES = 1540
MIN VALUE = 0
MAX VALUE = 157
ARITH MEAN = 27.4
ARITH S.D. = 4.55
MEDIAN = 26.7
MODE = 24
SKEWNESS = 0.519
KURTOSIS = 209
CLASS INTERVAL = 20

Do you want a printout ?

KIDD CREEK MINES LTD
Frequency histogram
TITLE ... BLOCK

CUMULATIVE FREQUENCY TABLE

INTERVAL	CUM FREQ %
0-20	15.13
20-40	37.34
40-60	71.86
80-100	88.19
100-120	89.32
120-140	92.40
140-160	100.00

KIDD CREEK MINES LTD
Cumulative frequency plot
Title ... Block

Figure 73. Screen display-printer output for proposed interactive statistics-histogram-cumulative frequency program

SELECTED REFERENCES

The following is a list of selected references from which much of the information presented during the workshop was derived.

Andrews-Jones, D. A., 1968. The application of geochemical techniques to mineral exploration: Colo. School of Mines, Mineral Industries Bulletin, Vol. 11, No.6, 31 p.

Fletcher, W. K., 1981. Analytical Methods in Geochemical Prospecting: Handbook of Exploration Geochemistry (G. J. S. Govett, editor), Vol. 1: Elsevier, New York, 255 p.

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