GGY 4119 – MINING GEOLOGY

GEOCHEMICAL EXPLORATION; Trace elements, dispersion, sampling, data compilation and interpretation

<u>Objective</u>

- The student should be able to understand the steps followed in geochemical exploration.
- Be able to manipulate and interpret geochemical data.

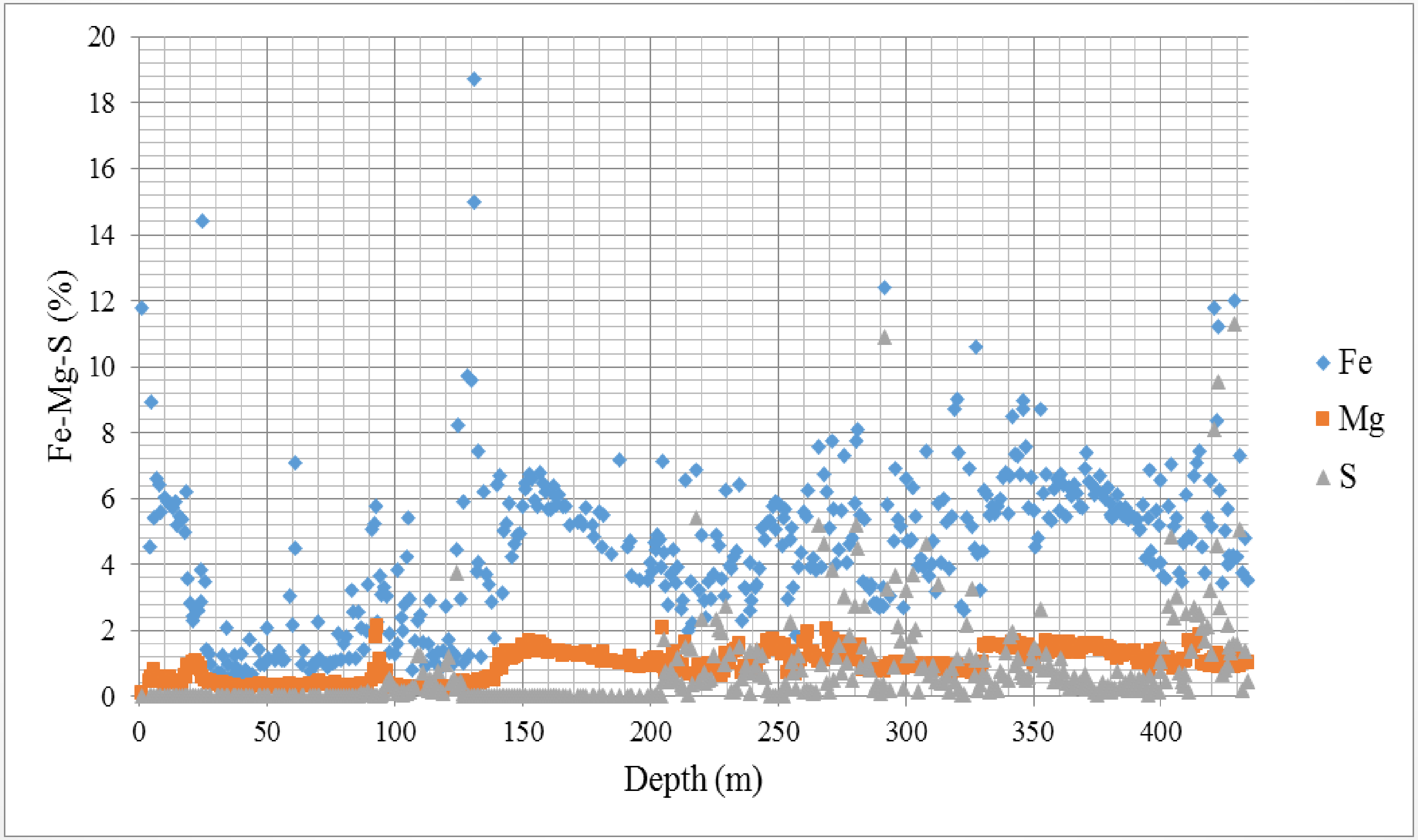
Acknowledgements

The contents of this presentation are mostly taken from articles/notes written by the following scholars;

- M. Aspandiar
- H. E. Hawkes
- B. Musonda
- W. M. White
- I. Nyambe

Objective of Exploration

To detect a geochemical or geophysical signature which when interpreted can provide a guide to finding **Ore**



Geochemical exploration: Concepts

- The use of chemical properties of naturally occurring substances (rocks, soils, stream sediments, waters and vegetation etc.) as aids in the search for **Ore deposits.**
- Mineral deposits represent *anomalous* concentrations of specific chemical elements.
- Most mineral deposits are surrounded by halos of abnormal **trace-element** concentrations in the adjacent and enclosing rocks, and in other naturally occurring substances.
- This halo represents the distribution of elements which formed as a result of **dispersion**.

Classification of geochemical anomalies

- **Primary Anomalies**
- These result from outward dispersion of elements from mineral-forming solutions.
- The “high” concentrations of metals surround the deposit and the dispersion of metals laterally or vertically along fractures may result in a leakage “halo” that extends hundreds of feet away from the deposit.
- Halos of this type are especially useful in prospecting because they may he hundreds of times larger than the deposit they surround and hence are easier to locate.

- **Secondary anomalies**
- These result from dispersion of elements by weathering. Some primary minerals, such as cassiterite, are resistant to chemical weathering and are transported by the streams as fragmental material.
- Other minerals may be dissolved and the metals may be either redeposited locally or carried away in solution in ground and surface waters.
- Some of the metal in solution may be taken up by plants and trees and can be concentrated in the living tissue.

Trace Elements

- Elements of the Period table are grouped into two classes; Major and Trace elements
- Trace elements are chemical elements present or required only in minute amounts or….
- Those elements that are not *stoichiometric* constituents of phases in the system of interest
- Trace elements are useful for providing geochemical and geological information out of proportion to their relative abundance.
- Present in concentrations <0.1%, expressed in ppm or ppb

- From the periodic table of elements, 6 elements, O, Ca, Fe, Si, Mg and Al make up 99.1% of the **silicate Earth**.
- If we include the **Core** and consider the composition of the entire Earth, only Ni and perhaps S need be added to the list. The remaining elements can be considered trace elements.

- **Indicator element**: This is the element whose concentration in the sampled material may indicate the presence of a given type of mineral deposit
- **Pathfinder element**: This is an element which is associated with an indicator element and whose properties are such that it can easily indicate to us the presence of a mineral deposit of a given type

Target Element	**Pathfinder Element**
Au	As, Sb, W, Se, Ba, Cu, Te, Bi
Cu, Pb, Zn	Ag, Se, Te, As, Sb, Bi, Mo, Mn
Ni	Cu, Co, Pd, Pt, Te

- Lets look at three, though there are several, *characteristics* of these elements that are useful in the search for ore deposits;
- *Variations* in the *concentrations* of many trace elements are much larger than variations in the concentrations of major elements
- In any system there are *far more trace elements than major elements*
- The range of *behavior* of trace elements is large and collectively they are *sensitive to processes* to which major elements are insensitive.

Dispersion

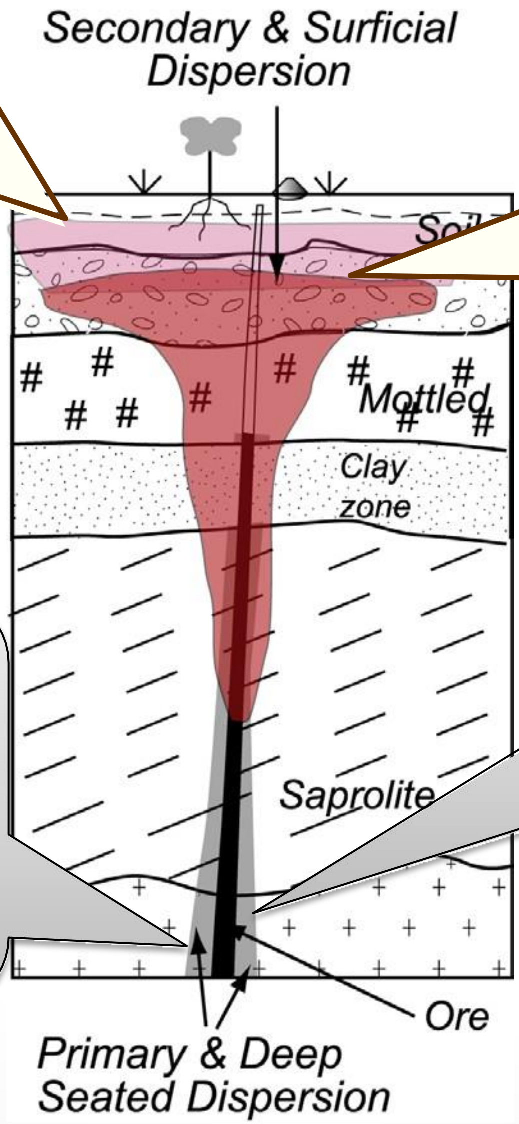
- This the movement of earth materials from one chemical environment to another
- The movement is in patterns that reflect both the abundance of the element in the material and the chemical equilibria characteristics of the local environment.
- In the literature of geochemical exploration, these patterns of movement and distribution are know as dispersion patterns.

- Dispersion patterns in geochemical survey data appear as areas where the abundance of an element is higher than the surrounding areas.
- They can be the effect of special features of the environment that cause local enrichments of the element from source material of background composition.

Geochemical Dispersion Types & Environments

Surficial
Surface processes of weathering, erosion and deposition disperse or concentrate elements – geochemical dispersion lecture

Secondary Dispersion
Distribution of element and patterns due to later processes (weathering related)



Deep Seated
Elements are fractionated or concentrated due to magmatic or hydrothermal environments – Ore geology

Primary Dispersion
Dispersion relating to movement of element due to magmatic or hydrothermal processes

Typical Geochemical Prospecting Program

- A full-scale geochemical prospecting program for metals would include the following stages:

➢ Preliminary evaluation of areas, selected on the basis of available geological data, by sampling and testing intrusive, metamorphic, and sedimentary rocks and by noting the presence of mineralized zones. In this way, a metallogenetic province can be identified.

➢ Primary reconnaissance and orientation surveys, based on sampling major drainage basins, using water, stream sediment, lake sediment, and heavy-mineral surveys.

➢ Secondary reconnaissance surveys based on detailed testing of drainage basins containing anomalous values. Poorly drained areas can be tested by widely spaced sampling of soil and ground waters.

- Follow-up surveys along dispersion trains or fans to determine the cutoff points and the extent of dispersion patterns. These surveys are normally a combination of stream sediment, heavy mineral, water, and soil testing, but biogeochemical surveys may also be useful. Priority for follow up surveys should be based on the presence of favorable rocks and geological structures, favorable geophysical indications, and intensity of the geochemical anomaly.
- Detailed surveys carried out in the vicinity of the suspected metalliferous source by soil or vegetation sampling at closely spaced intervals. Interpretation of the results at this stage generally suggests sites for trenching, sinking of shallow shaft, or drilling to locate the precise source of the body giving rise to the geochemical anomaly.

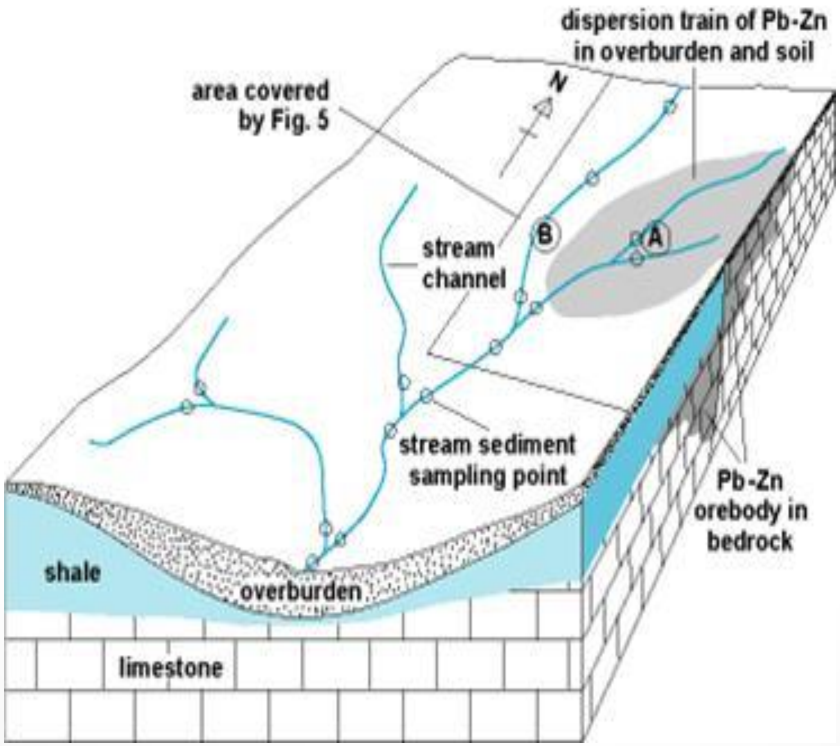
Precautions During Sampling

- Clean sampling equipment before sampling (paint, residue)
- Avoid cross contamination – clean sampling equipment between samples
- Sampling bags > plastic, calico and paper
- Correctly label sample bags
- Avoid jewelry and other metal objects

Sampling – Medium and Techniques

- ***Rock surveys*** – The elements forming the dispersion pattern in this sampling medium may be either evenly distributed throughout the rock mass or segregated as clots of minute fracture fillings.
- One or several rock types may be selected for sampling and analyzed for various elements. The distribution of the volatiles such as chlorine (Cl), fluorine (F), water (H_2O), sulfur (S), and CO_2 in intrusives with associated mineralization has received some attention as an indicator.
- Geochemical maps are compiled from the analyses, and contours of equal elemental values are drawn. These are then interpreted, often by using statistical methods, in the light of the geological and geochemical parameters.
- Under favorable conditions, mineralized zones or belts may be outlined in which more detailed work can be concentrated.

- ***Stream sediment surveys*** – The most efficient way of establishing the existence of anomalies in a large area is by means of a stream sediment survey
- In a stream sediment survey one assumes that the indicator elements have been transported from the source to the stream channels in either solid state or dissolved state.



- Need To Consider…
- Sampling material
  - Water – Fine grained sediment
  - Coarse grained – Heavy minerals
- Sampling density
  - Number of samples per km^2 (1st – 2nd order)
  - For example, 1 per 2 km^2 or 1 per 4 km^2
- Analysis – Bulk OR partial leaches to increase contrast
- Commodity – Au has its problems
- Climate – Dry (arid) vs Wet (humid)

- Climatic Conditions
- Mode of dispersion varies depending on climate (dry vs wet)

– Arid, dry regions

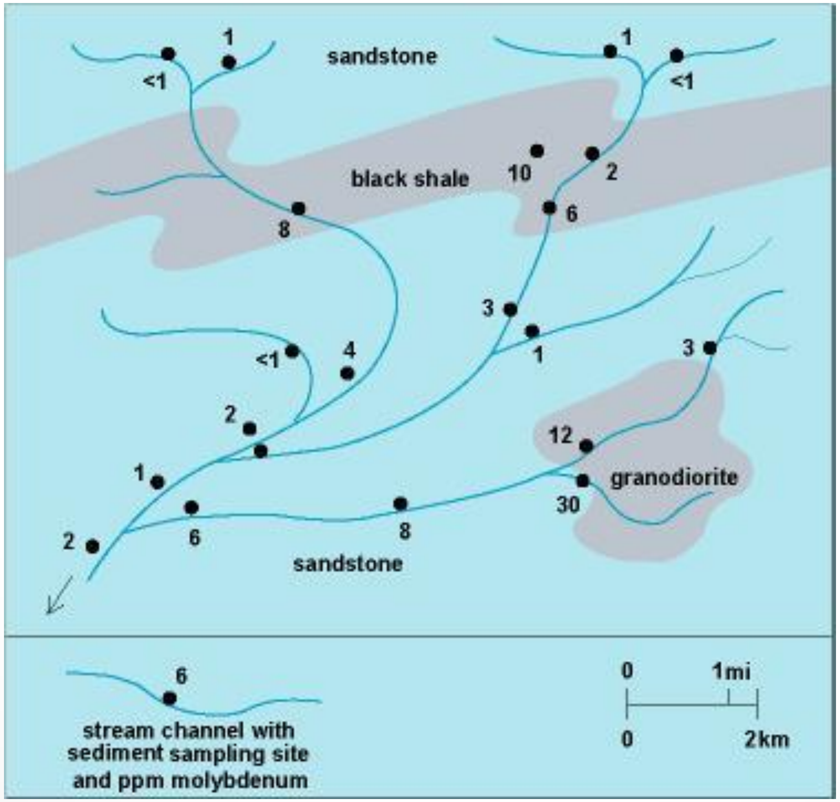
– Humid, wet regions

- Dispersion type

– Mechanical (physical, grain size decrease) = ARID

– Chemical (solute – adsorbed onto clays & oxides) = WET

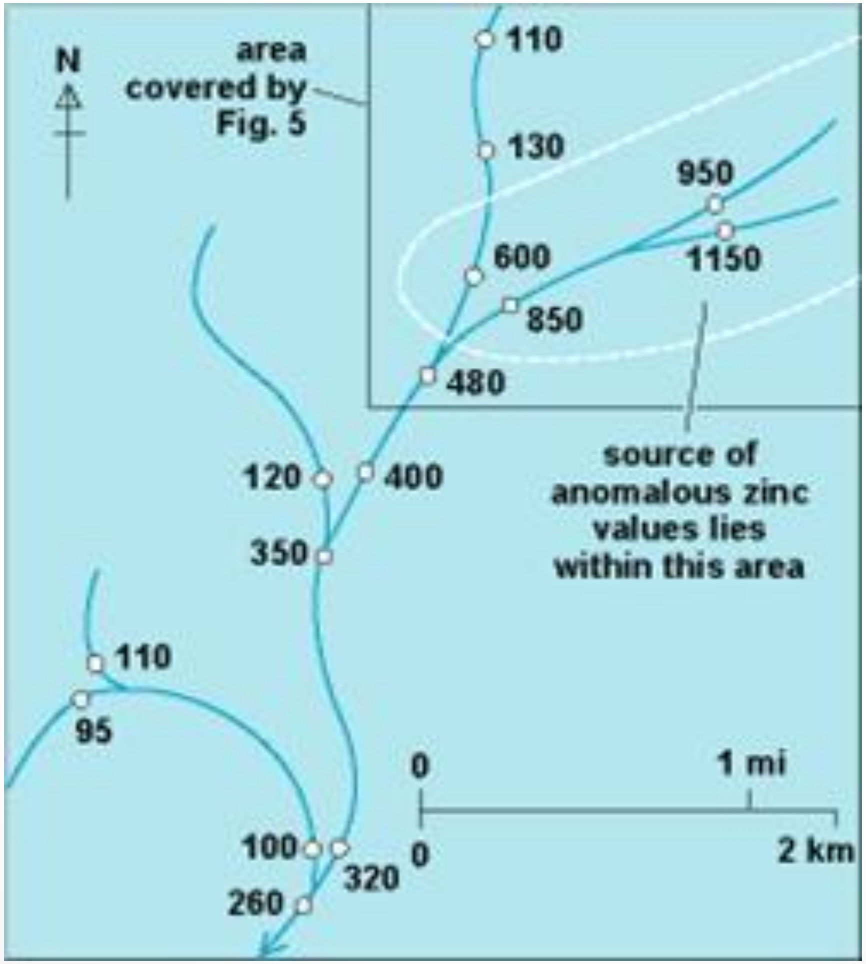
- The sampling pattern used depends upon the distribution of streams, the scope of the survey, the accessibility of sampling sites and the expected decay pattern of the anomalies.
- Useful medium to sample when heavy-metal mineral content of sediments is to be measured.



- Sample is collected from the surface of the bedrock beneath the stream either by digging a pit or augering a hole.
- Sample is collected using waterproof containers; heavy paper envelops made with waterproof glue or small aluminium containers are most satisfactory.

Stream sediment sampling, the Kafue River

- After collection of the samples the samples are dried and sieved to a given mesh size (normally to minus 80 mesh). After preparation the samples are analysed using an appropriate analytical method.



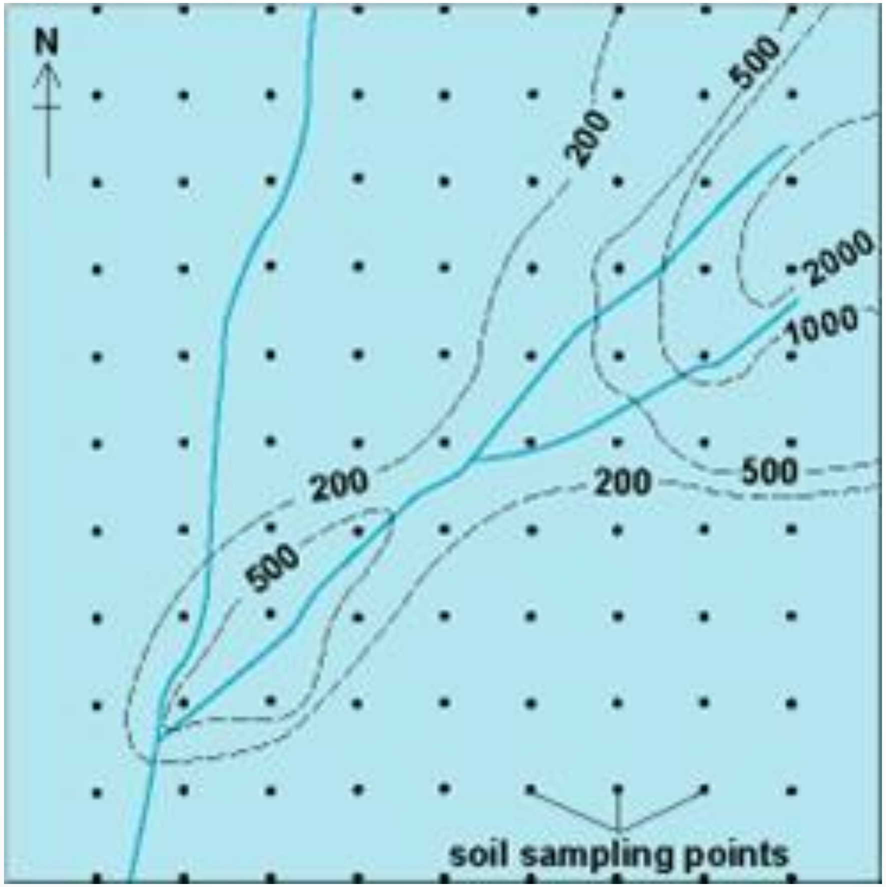
- ***Water surveys*** – Water samples are normally collected in very clean polyethylene containers from stream channels, bore holes, lakes and springs and a map of the value is prepared.
- An increase in the metal content of the water upstream may indicate approach to a mineralized zone
- Despite being useful, this sample medium presents a unique set of problems in that traces of elements is relatively unstable and pose to be a source of error.

Surface water sampling

- The major problem lies in the storage of a water sample.
- Ions tend to be removed from the solution and get adsorbed to the walls of the container.
- The formation of FeOH precipitates can also cause the removal of ions from the solution.
- Analyses should therefore be made on site using portable analytical kits.
- The parameters which are commonly measured in the field include: pH, conductivity, dissolved oxygen, Eh, Undifferentiated heavy metals, SO_4^{2+}, Cu, Mo, and Zn.

- ***Soil surveys*** – Sampling and analysis of soils is one of the most widely used methods in mineral exploration. It is the most efficient and reliable method of locating zones of mineralization.
- In stony soil it is usually easier to collect a sample with a pick and shovel for shallow hole.
- In clay soils and also for deeper holes, a soil auger is more suitable.
- The sampling pattern is selected on the basis of the geometrical properties (size, shape, orientation) of the target.

- The sampling pattern is selected on the basis of the geometrical properties (size, shape, orientation) of the target.



Topsoil sampling

Lower soil sampling

- Under favorable conditions, the highest values are centered over a deposit, but more generally the dispersion pattern is a train or a fan that requires careful interpretation to locate its source.
- In soil analyses the fine fraction is generally analyzed for the chemically dispersed elements, whereas for heavy and resistant minerals a coarser fraction is used.
- Samples with a mass of about 200 to 400 g are usually collected at the appropriate depth interval using auger drills or other tools and placed in water resistant kraft paper envelopes
- The standard procedure adopted for such surveys has been to collect fines (- 80 mesh) or <2mm in diameter and grind before analysis.

- ***Vegetation surveys*** – The essence of a biogeochemical survey is to locate a biogenic dispersion pattern which is produced by the biogeochemical cycle.
- Samples of vegetation for chemical analysis should be taken far enough above the ground to be clear of contamination, mostly from rain spatter.

Cassava leaves sampling

- Biogeochemical surveys are most suitable for elements which tend to show a high contrast such as Pb, U, Co and Mo.
- Experiment has shown that it is necessary to confine a geochemical plant survey to samples taken from the same organ of the same species.
- For most analytical procedures, 5 grams sample size is required. The most commonly used containers are lightweight paper bags.
- The samples should be dried or ashed prior to chemical analysis. The data should be processed in the same way as soil data.

Analysis
Sample Preparation

- **Target and pathfinders**
  - Target only? Target & pathfinders? How many?

- What type of **analytical technique**?
  - Depends on elements being analyzed & cost
  - Pre-treatment required
  - Digestion & Fusion (Fire Assay, Acid digests - Aqua-Regia, Four acid)
  - Analytical method and package (ICP-MS, AAS, ICP-AES)

- What will **cost**? **How good is the lab?**
  - Quality control (QC) and quality assurance (QA)
  - Insert own **standards, duplicate, blanks** with samples
    - – authenticity of the analysis (can you trust the results?)

Analysis
Sample Preparation

Does the sample require **drying**?

- Generally yes.

Does the sample require **screening** / sieving?

•Depends. Soils/lags yes. < 80#. Cost $45 per/h

Does the sample require **crushing**?

•Only if they are too coarse. Cost $0.50 per/s

Does it need to be **pulverized**?

•For most samples yes. Achieve <75 μm. Cost $4 per/s

Analysis
Digestions & Fusing

AQUA REGIA Digest

- 3 HCl: $1HNO_3$
- Dissolves most regolith minerals

FOUR ACID – "Near Total" Digest

- $HF-HClO_4-HNO_3-HCl$
- Dissolves most minerals except some resistates

LITHIUM BORATE Fusion

- Dissolves resistate minerals

CYANIDE LEACHES

- Mainly for Au

COLD EXTRACTABLE LEACHES (HCl, Na-pyrophosphate, hydroxyamine)

Only attack specific minerals or "amorphous" minerals

Analysis
Analytical Method & Packages

Ore Types

- Gold & PGEs: Fire Assay, INAA
- Base Metals: AAS, ICP-MS, XRF
- Ferrous: XRF

Dry Methods: Require only powder prepared via fusion

- X-Ray Fluorescence (XRF)
- Instrument Neutron Activation Analysis (INAA)

Always state **sample digestion (prep)** AND **analytical technique**

Wet Methods: Require dissolution of sample via acid digests

- Atomic Absorption Spectrometry (AAS)
- Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)
- Fire Assay

Analytical Method & Packages

Description: 27 elements by Four Acid Digestion

ICP-AES

Ag(0.5-100), Cd (0.5-500), Mn (5-10,000), Sb(5-10,000), Al (0.01%-25%), Co (1-10.000), Mo (1-10,000), As (5-10,000), Na (0.01%-10%), Ti (0.01-1%), Cu (1-10,000), Ni (1-10,000), V (1-10,000), Fe (.1-25%), Pb (2-10,000), Zn (2-10,000)

$16 (complete package) or $11 plus 0.35/element

AAS

Ag (1-100), Cd (1-10,000) Mn (5-10,000), Z (5-10,000), As (20-10,000), Ni (5-10,000), Cu (5-10,000), Pb (5-10,000), Fe (0.01-15%), Sb (5-10,000)

$5.50 plus 1.50 per element

ICP-MS

Ag (.5-100), Cd (.5-10,000) Mn (5-10,000), Z (5-10,000), As (20-10,000), Ni (5-10,000), Cu (1-10,000), Pb (5-10,000), Fe (0.01-15%), Sb (5-10,000)

$11.0 plus 0.35 per element

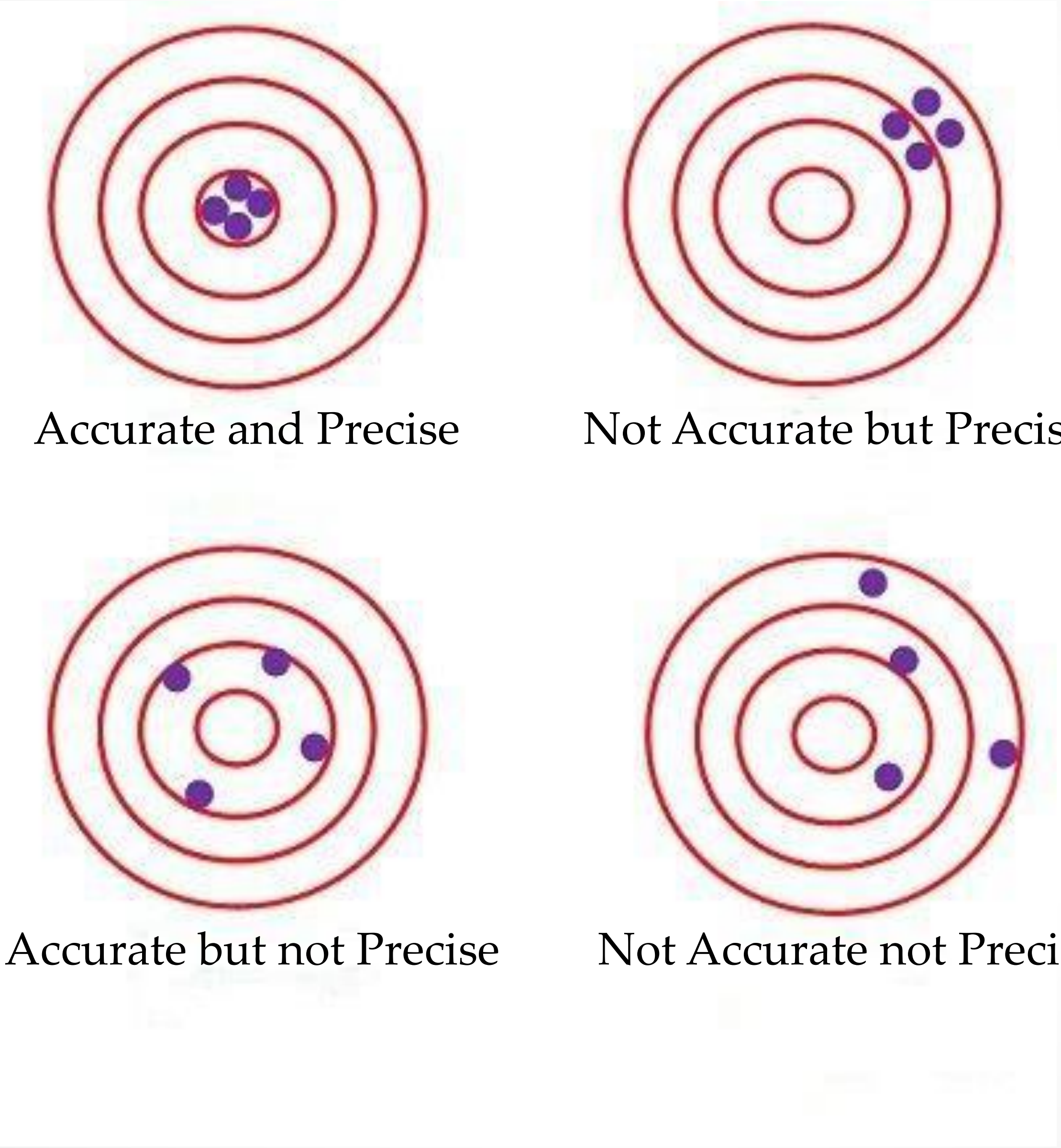
Laboratory analysis

- The samples are analysed at the laboratory using a wide range of techniques depending on cost, number of samples being analysed, number of elements etc.
- During the entire sampling chain, errors are introduced.
- We need to check if these errors are within acceptable limits or the uncertainty in the results is suitable for intended use.
- A Quality Assurance Quality Control (QAQC) program allows you to evaluate the uncertainty in the results and check if it is sound for intended use i.e. Is the data FIT FOR PURPOSE?

Precision, Accuracy & Bias

- For QAQC we need to measure precision, accuracy and bias.
- Accuracy – the degree to which an analysis or mean for a set of analyses approach a "true" value. In other words it is the closeness of the measured value to a standard/true value
- Precision – it is the estimate of the reproducibility of the sampling and analytical system.
- Bias – a systematic error inherent in a method or caused by some artifact of the sampling system.

Precision, Accuracy & Bias



So…how do we achieve QAQC??...details in sampling theory lecture

- QAQC is achieved by
- Use of STANDARDS; material of known content to assess the accuracy and precision of assay results
- Use of DUPLICATES; samples to assess the precision (i.e. repeatability) of assay results
- Use of BLANKS; to assess lab contamination

Geochemical data:
Compilation and Interpretation

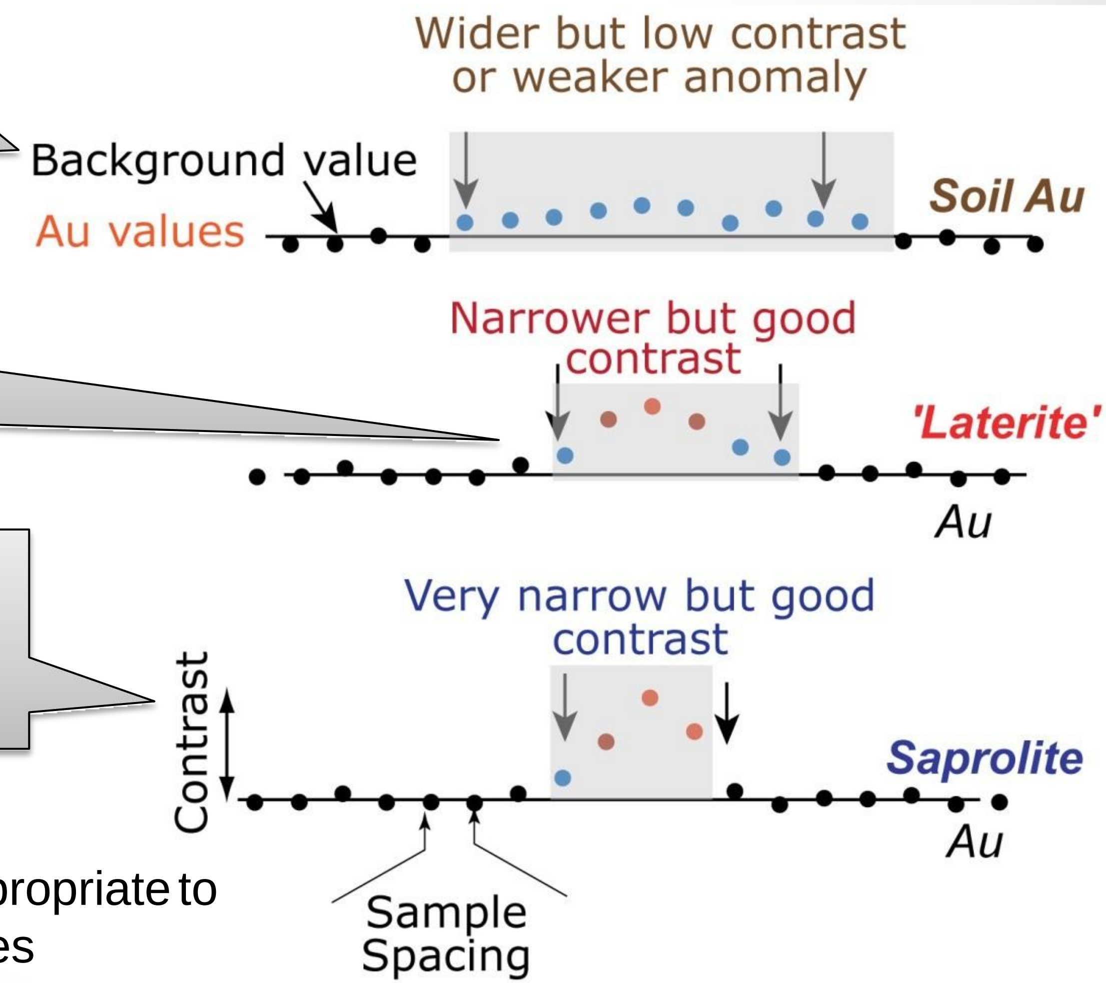
- The geochemical data obtained from these analyses is processed, plotted and interpreted.
- Clear and concise graphic plots of geochemical data make the task of interpretation easier.
- The most common method used is *Statistics*. The essence of statistical data analysis is to distinguish between anomalous values and background values.
- A number of graphical/statistical methods are available for examination of a data set for discontinuities in the distribution: The histogram method and the cumulative frequency curve method.

Anomalies, Background & Contrast

Background concentration: normal geochemical patterns (i.e. from unmineralised area), for a particular sample Statistically – geometric mean

Threshold is outer limit or upper limit of normal background variation or background population

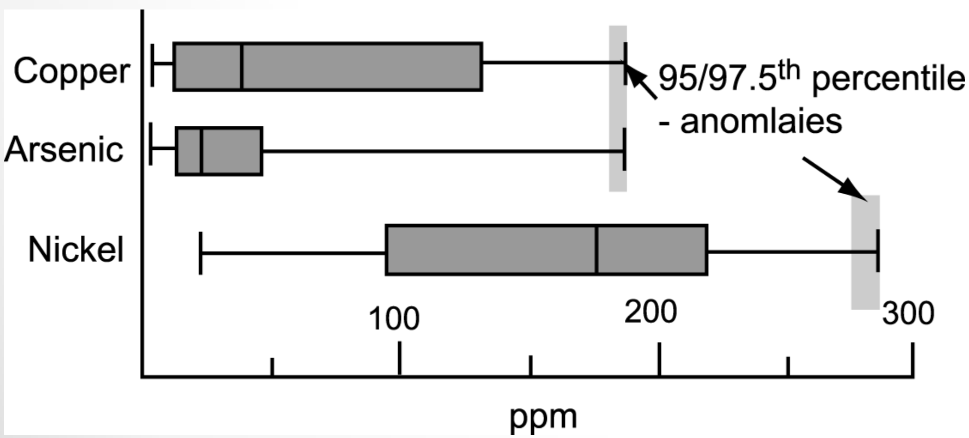
Contrast: the ratio of the anomalous value to background sometimes also referred to as **anomaly ratio**

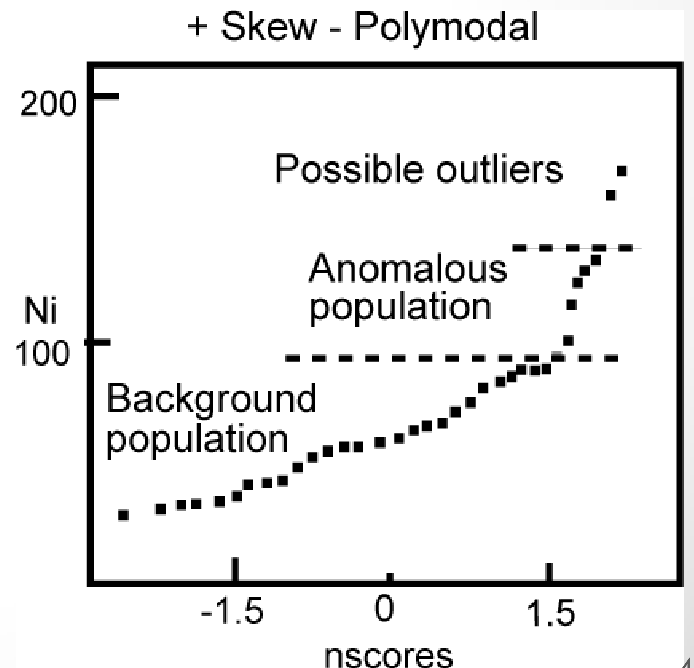


Statistics of data set is most appropriate to identify background and anomalies

Data Analysis To Find Anomalies

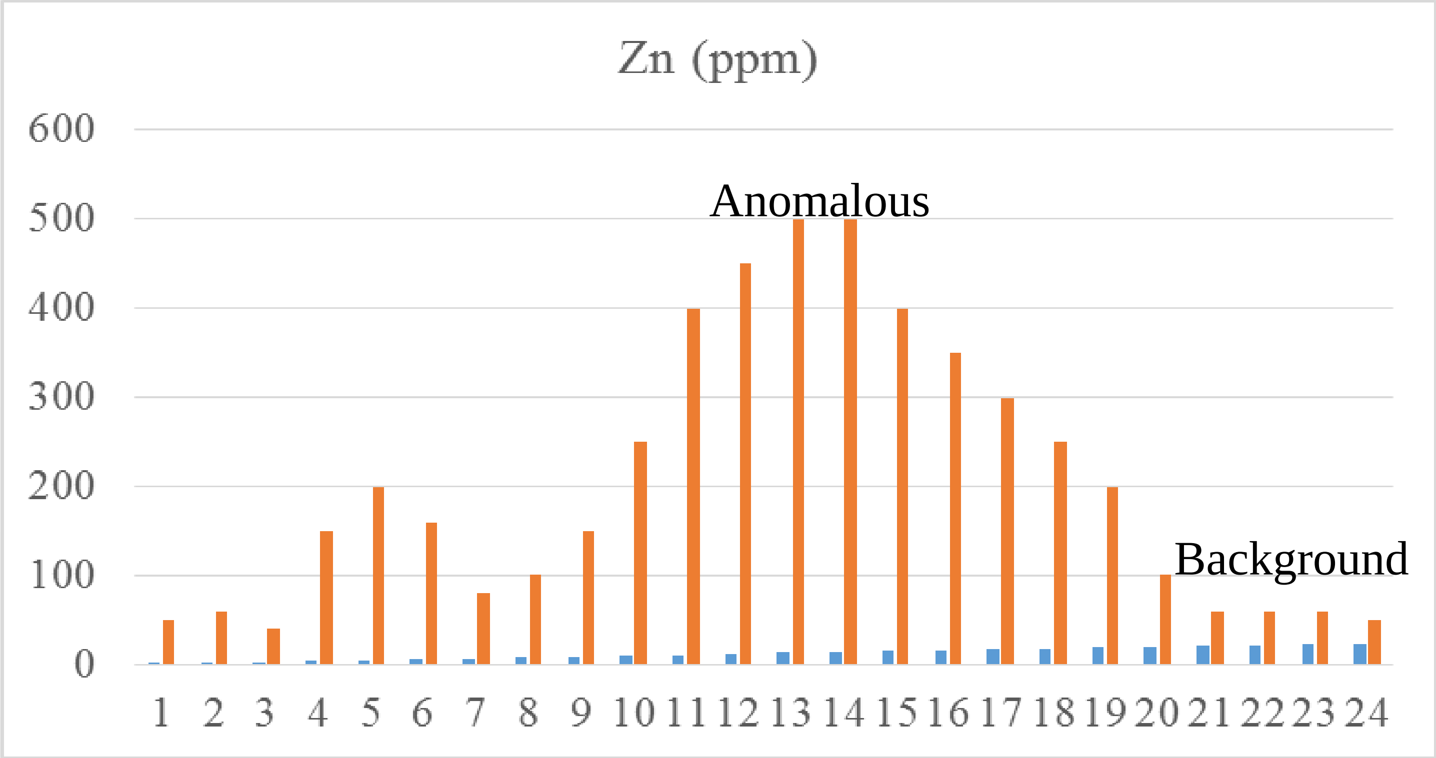
- Data received from labs – check validity/standards
- Rank the data – Percentiles
  - 97.5th   95th   90th percentiles
- QQ Plot or normal probability plot
- Dissect populations – anomalous – find cut offs





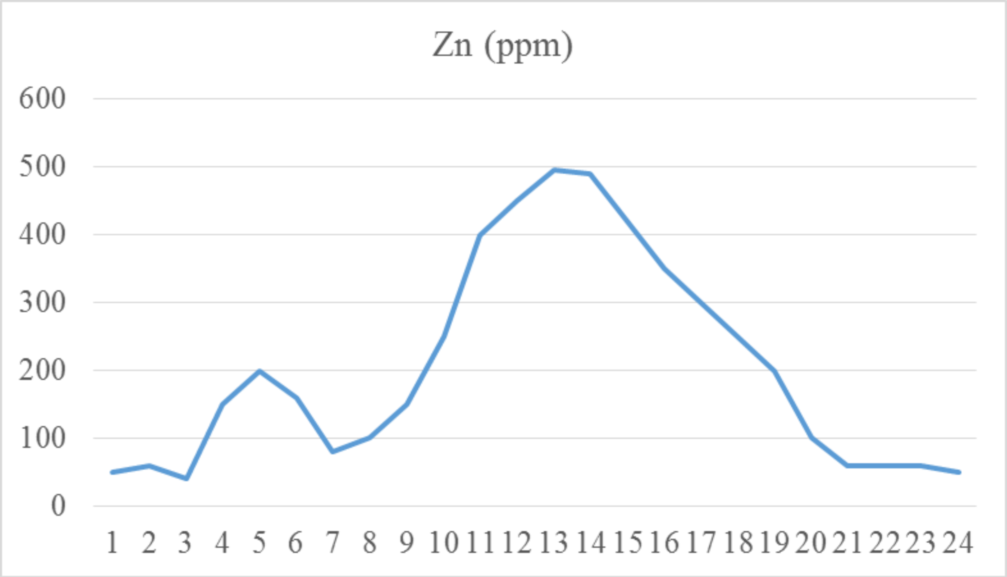
Histogram

- The Histogram method involves the construction of a histogram using the values in a data set and determining a value which corresponds to a major break in the distribution and that best represents the boundary value between anomalous values and background values.

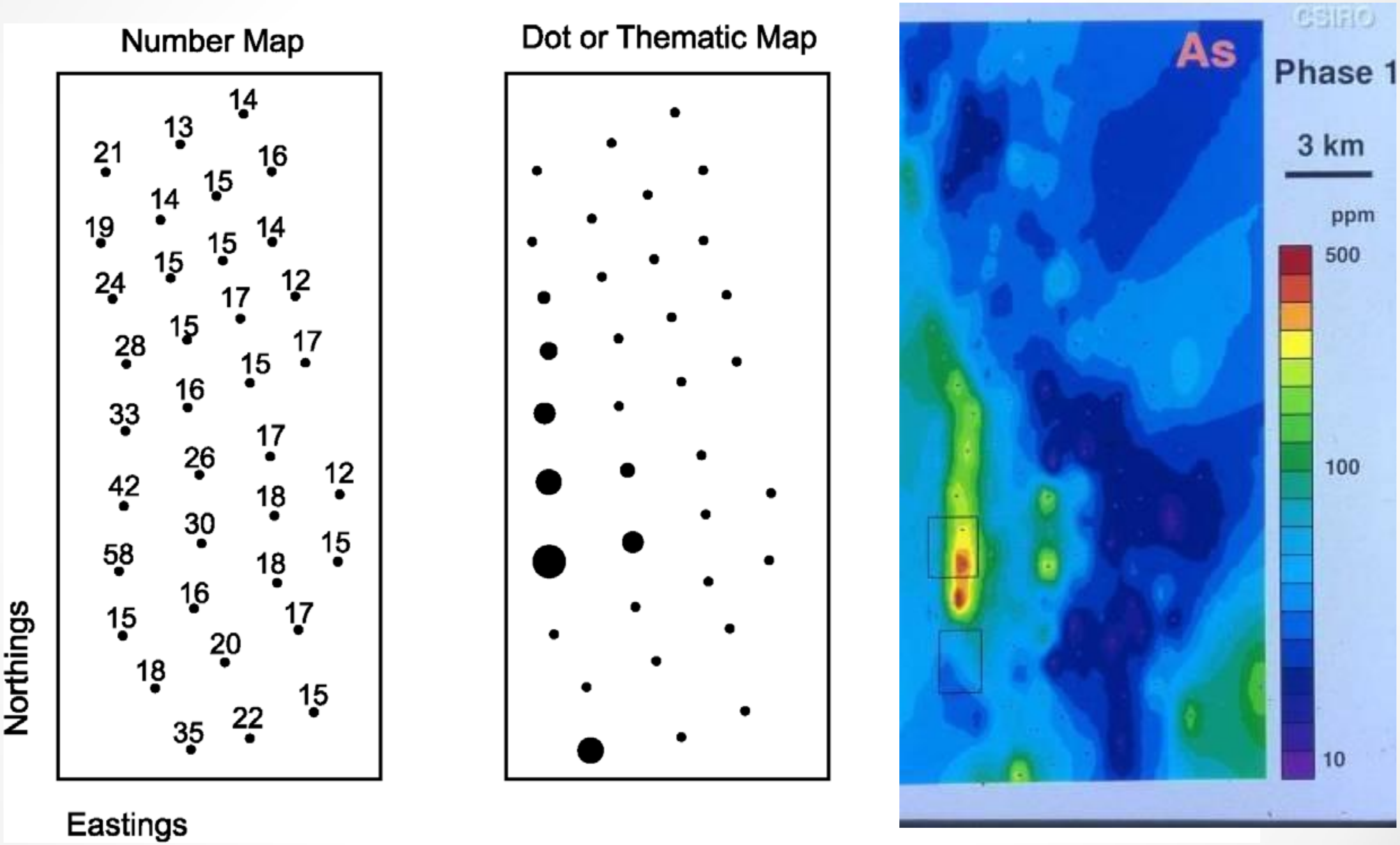


Cumulative frequency curve

- The cumulative frequency curve is perhaps the best method of splitting a data set into two sub-populations of background values and anomalous values
- Some data sets may have more than two sub populations and using this method it is possible to split any data set into the actual number of sub-populations present
- In geochemical exploration we are interested in the subset of the data set which contains anomalous values



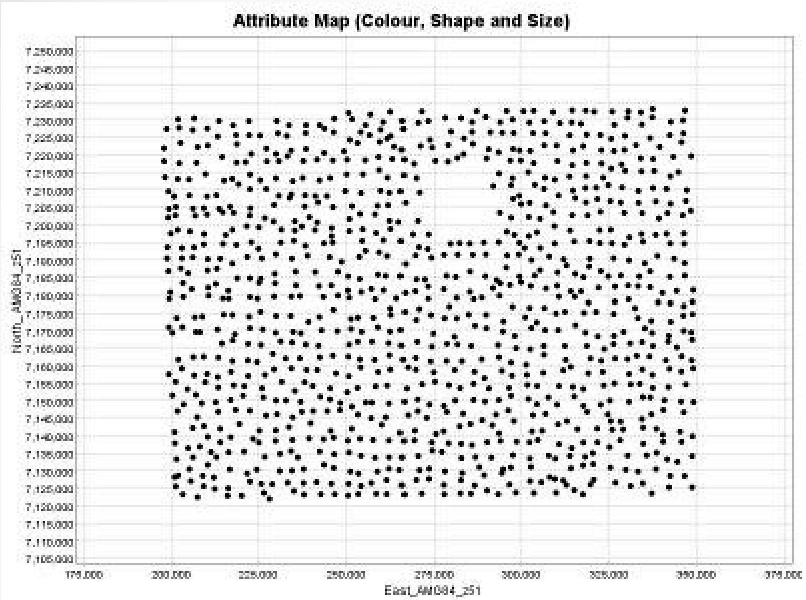
Spatial plots of data

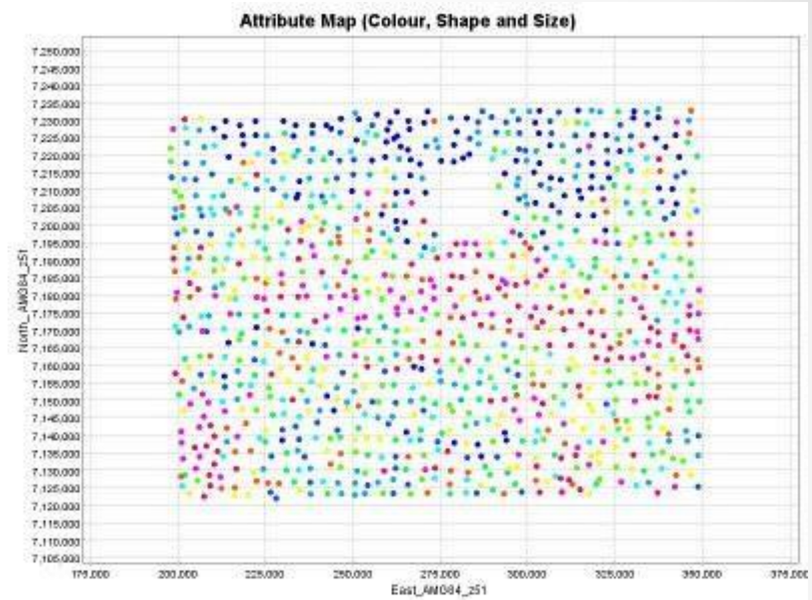


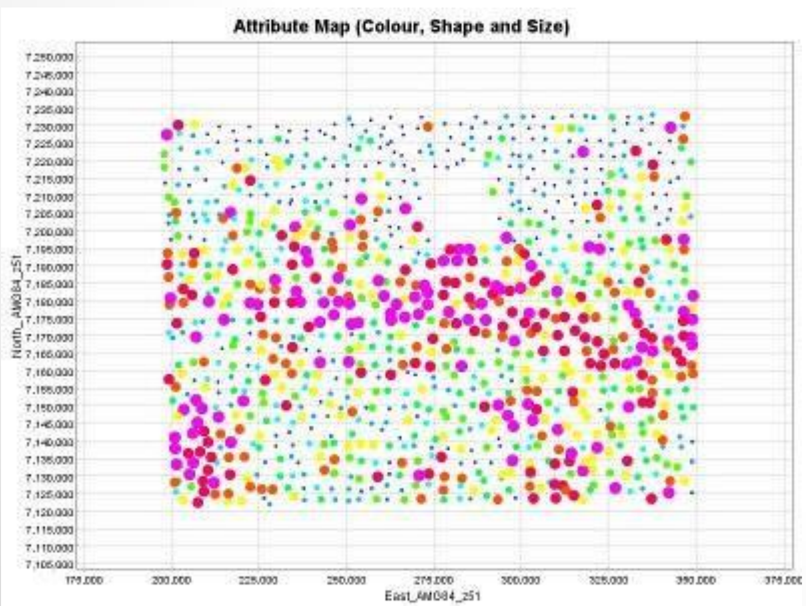
Increasing degree of spatial variance of representation of true value of data

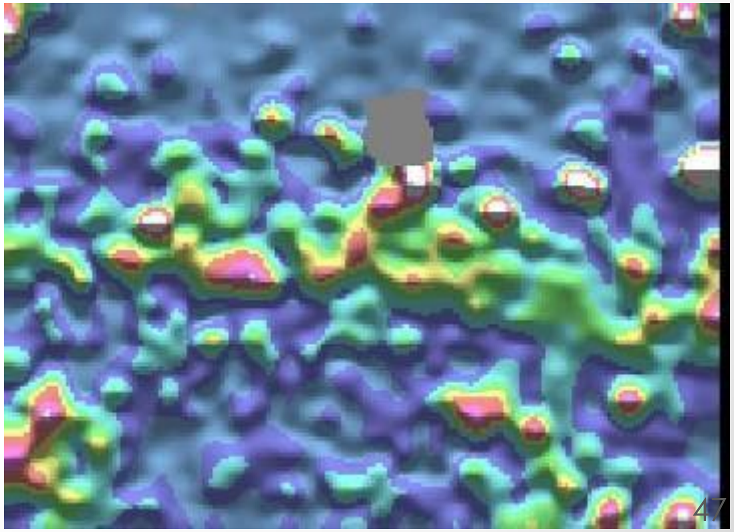
Increasing reliance on computer interpretation

Spatial Plots – Visualization Enhancement



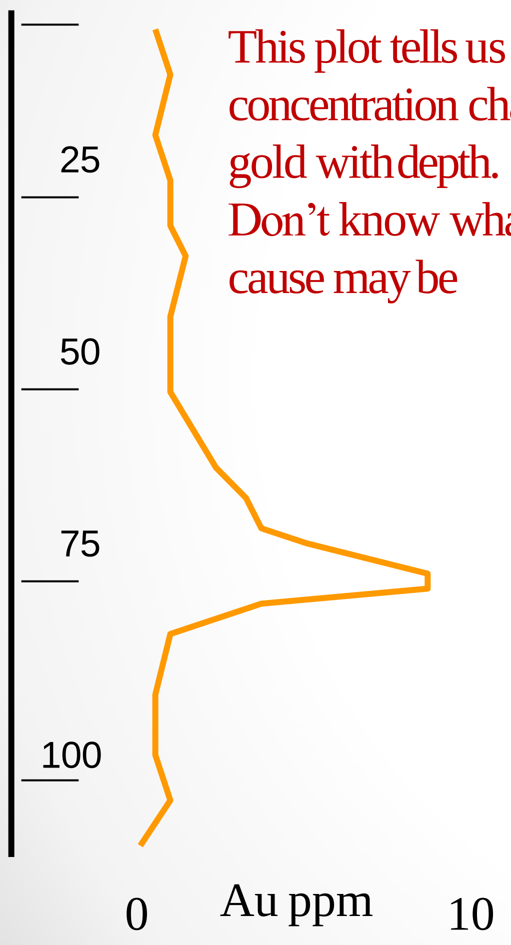






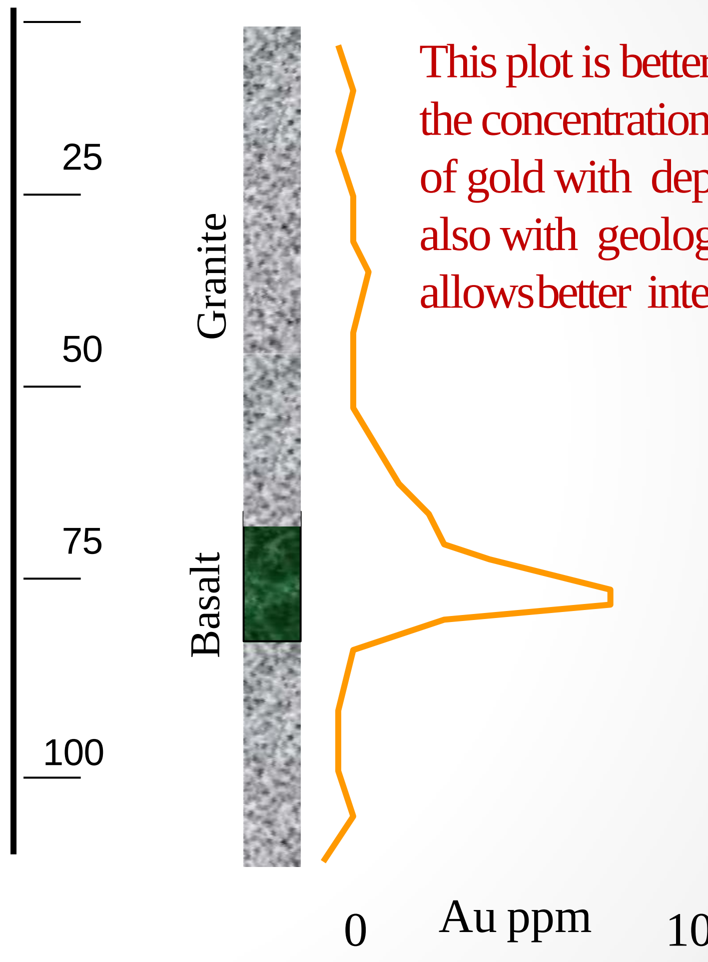
Scatter Plots – Downhole Line Plots

Gold values with depth



This plot tells us the concentration change of gold with depth. Don't know what the cause may be

Gold values & geology with depth



This plot is better - tells us the concentration change of gold with depth but also with geology = allows better interpretation

- Accurate interpretation of geochemical survey data is the final step in effective geochemical exploration.
- Skill in interpreting geochemical data must depend;
- First upon general familiarity with the many factors that contribute to the formation of geochemical anomalies, and
- Secondly on a specific knowledge of the balance of these factors in the area under study.
- If mineralized ground is discovered, recommendations for further examination by diamond hole drilling are made
- ***No hard-and-fast rules can be given for the interpretation of geochemical data.***