Soil Survey and Lithogeochemical Techniques in Mineral Exploration

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DOI: https://doi.org/10.51584/IJRIAS.2024.90336

Received: 08 March 2024; Revised: 19 March 2024; Accepted: 23 March 2024; Published: 17 April 2024

ABSTRACT

This paper investigates the critical roles of soil surveys and lithologic evaluation in identifying potential mineral resources. Soil surveys involve the systematic mapping, examination, description, and classification of soils within a defined area. Through targeted sampling and laboratory analysis, these surveys can reveal the concentration of metals in the soil. By analyzing these metal signatures, geoscientists can infer the underlying geology and identify areas with a higher likelihood of hosting valuable mineral deposits. Lithologic evaluation complements soil surveys by focusing on the physical characteristics of rock units exposed at outcrops, in hand samples, or cores. Observable with the naked eye or a magnifying lens, these characteristics include color, texture, and structural features. Lithogeochemistry, or rock geochemistry, builds upon this foundation by analyzing the chemical composition of the bedrock. This analysis aims to identify spatial patterns of elements typically associated with specific types of mineral deposits. By integrating the findings from soil surveys and lithologic evaluations, geoscientists gain a comprehensive understanding of the subsurface environment, enabling them to prioritize areas for further mineral exploration activities. This paper delves into the fundamentals of these techniques, highlighting their strengths and limitations in the context of mineral resource exploration.

Keywords: Survey, lithogeochemistry, mineralization exploration

INTRODUCTION

Geochemical prospecting for mineral deposits is an ancient technique. For millennia, prospectors have sought Fe and Cu stains on rocks, which result from the oxidation of sulfide mineral deposits and the subsequent dispersion of the products, as possible indicators of mineralization (Rose *et al*., 1991). Panning for Au and other heavy minerals is also an ancient and successful geochemical prospecting method. Most applications of geochemistry in mineral exploration focus on detecting and mapping patterns in the chemical composition of the lithosphere or biosphere that can be linked to the effects of mineralization. In designing geochemical exploration surveys, various combinations of sampling media, sample processing, geochemical analysis methods, and data processing and interpretation models can be selected from a wide array of options (David and Rob, 2013). Most geochemical exploration studies in the primary environment may be classified as litho-geochemistry.

The purpose of many litho-geochemical surveys has been the identification of element enrichment or depletion in zones surrounding mineralized rocks. Alteration of wall rock commonly provides the most discriminating evidence of geochemical changes (Boyle and Jonasson, 1973; Large *et al.* 2001). The redistribution of chemical elements at, or near, the earth's surface due to weathering, transportation, sedimentation, and/or biological activity is classified as secondary dispersion. Mapping the effects of such processes is used to detect concealed or buried mineralization (Cameron *et al.*, 2004). Weathering is essentially the process by which minerals that are normally stable within the crust break down near-surface under the effects of water (hydrolysis and oxidation) to form supergene or secondary minerals, with the loss of some more mobile elements. The resulting material is commonly referred to as regolith. These components may host elements dispersing from underlying mineralization. Secondary halos aid in the search for deposits as they normally cover a greater area, and the chance of a chemical survey selecting a sample from these areas is greater than from a primary halo area. Subsequently, the secondary halo may not contain the "metal" for which a geochemical survey is searching but other "marker" elements. These are commonly employed during geochemical surveys. In mineral exploration, soils and other near-surface geochemical samples are frequently collected to provide information on the underlying bedrock (litho) geochemistry.

Several researchers have affirmed the potency of soil survey and litho-assessment procedures in mineral exploration. Ajayi (1988, 1995), Omoyinoye and Adekeye (2013), Adesiyan *et al*. (2014), Turnbull (2015), Adepoju (2019), Adepoju *et al*. (2021), and Alao-Daniel *et al.* (2023). Ajayi (1988) carried out a statistical analysis of soil sample survey results from the Ife-Ilesha area and noted that both simple statistical and R-mode factor multivariate analytical techniques were useful aids in the interpretation of reconnaissance soil sample data. Ajayi (1981) later noted that the moving average and derivations from the trends using the moving average method reduced the effects of local variations in the regional geochemical data of the Ife-Ilesha gold field. Omoyinoye and Adekeye (2013) carried out detailed mapping and sampling of rocks and soils at Eruku and environs, Ilorin. The soil samples were collected from the B horizon at a depth of 20–25 cm. Twenty-five selected soil samples were analyzed for trace and rare earth elemental concentrations using ICP, INAA, MS, and ICP-MS analytical methods. The results showed an anomalous concentration of cassiterite, tantalite, and columbite minerals. These mineralizations are hosted by pegmatites that intrude on the country rocks in the study area. In order to follow up on some geochemical anomalies discovered in a regional stream sediment survey in parts of southwestern Nigeria, a medium-density geochemical soil survey was carried out in the Gbongan-Odeyinka area of Osun State, southwestern Nigeria, by Adesiyan et al. (2014). Results indicated that Pearson correlation study and factor analysis enabled separation of the 13 elements into the following three factors or metal associations: 1) Pb-Co-Ni-Fe-Cr-As-Mn-Cu; 2) Sn-Ag-Au-Cd; and 3) Zn-Cd, which were interpreted to reflect the influence of both environmental and mineralization factors on the soil of the study area. Turnbull (2015) collected soil samples at an 8 km-spaced grid across Southland and south Otago from the A soil horizon (0–30 cm) and a deeper sample (50–70 cm) at the B soil horizon. Concentrations of precious, base, and platinum group metals, as well as major, minor, and trace elements, were analyzed using XRF and ICP-MS. The results of this study showed that parent rock lithology is the main factor influencing the abundance and distribution of elements in the soils of southern New Zealand. Also, the deeper B-depth sample is less likely to have been influenced by human activities, and its chemistry best reflects the underlying geology, making it the preferred soil horizon for mineral exploration purposes. Adepoju (2019) examined the geochemical soil survey of base and precious metals in the Dagbala-Atte district, southwestern Nigeria. He sampled soils using a grid pattern and analyzed the concentration of base and precious metals, linking the suspected Cu-Pb-Zn-Ag mineralization to the rock types in the area. Adepoju et al. (2021) investigated the pedogeochemical survey for uranium mineralization in the Dagbala-Atte district, Igarra schist belt. Samples were collected at the B horizon and analyzed with ICP-MS. Results showed in the geochemical maps of the area that the strongest U anomaly occurred in the northeastern part of the district that is underlain by granitic gneisses with numerous unmapable granite-pegmatite veins, which possibly are the host of the U mineralization.

Alao-Daniel et al. (2023) carried out a soil survey in the Songbe area. Soil samples were collected by driving a 1-meter auger down to a depth of 50–80 cm into the ground after removing the topsoil to penetrate the B-horizon. The samples were subjected to standard preparation and treatment prior to geochemical analyses performed using XRF and LA-ICP-MS. After the results were interpreted, he concluded that multi-elemental chemical analyses using soil as sampling media is a vital tool to delineate underlying geology in the tropics and are an aid to geological mapping.

SOIL SURVEY

Soil Survey is a systematic mapping, examination, description, and classification of the soils in a given area (Brady and Weil, 1996).

Types of Soil Survey and Scales of Soil Maps

Exploratory Survey: This involves rapid road traverses made to provide information about unknown regions. Scales vary from 1:2,000,000 to 5,000,000.

Compilation Survey: This is soil mapping based on abstraction from other surveys. Scales are usually 1,000,000 or smaller. The National Soil Map of Nigeria belongs to this category.

Reconnaissance Survey (Low Intensity Detailed Survey): The established scale is 1:250,000, but maps of 1:500,000 to 1:120,000 are included. They are usually integrated surveys making much use of aerial photograph interpretations. Mapping units are mainly landform classes.

Semi-Detailed Survey (Medium Intensity Detailed Survey): The range is 1:100,000 to 1:25,000, typically 1:50,000. Aerial photo interpretation is combined with a substantial amount of field study. Mapping units vary from soil-landform classes to soil associations and series.

Detailed Survey (High Intensity Detailed Survey): Scale range is 1:25,000 to 1:10,000 inclusive and is produced mainly by field studies. Mapping units are soil series and phases of series.

Intensive Survey: Scales are larger than 1:10,000, usually 1:2,500 to 10,000, typically 1:5,000. Grid or regular traverse methods of field survey are used. Mapping units are soil series and phases.

Methods of Soil Survey

There are three main stages: pre-field preparations, field surveys, and post-field operations.

Pre-field preparations: These include collation and study of existing data of the area (maps, reports, topo-sheets, and analytical data), general field reconnaissance, aerial photo assemblage and interpretation, and design and planning of field survey.

Field survey: Activities include soil mapping operation and sampling technique leading to the production of a soil map.

There are two methods of field survey namely:

1. Free survey: The analyst uses his/her judgment of the objectives of the survey and all available aerial photos and ground evidence to locate profile pits of the most useful and representative sites. The number of profile pits depends on the requirements of the survey and the complexity of the soil pattern.

2. Grid survey: Observations are made at regular intervals along pre-determined traverses in the survey area.

Post-field operations: This involves sample preparation, sample digestion, sample analysis, and data analysis.

Sampling of Soil

Sampling is the process of collecting a small portion of soil from a location for subsequent analysis at a laboratory. The results obtained measure the concentration of metals in the soil and are used to infer the geology of the area. The sampling process begins with the definition of the project objectives and a stage which requires the analyst to clearly explain why the study should be undertaken. Selection of sampling strategy includes sample size determination. The decision regarding the number of samples required is determined by the objectives of the study, accuracy required, sampling design, size of the sampling target, and sampling and project budget.

Sampling Materials and Procedures

Sampling materials

i. Topographic Map

ii. Continuous flight (screw) auger

iii. Bucket auger

iv. Post hole auger

v. Sampling trier

vi. Split spoon sampler

vii. Soil core sampler

viii. Measuring tape

ix. Global Positioning System (GPS)

x. Ziplock plastic bags

xi. Field Notes

xii. Sample tapes

xiii. Spade or shovel

xiv. Scoop

Several types of augers are available; these include bucket or tube type, and continuous flight (screw) or post-hole augers. Bucket or tube type augers are better for direct sample recovery because a large volume of sample can be collected from a discrete area in a short period of time. When continuous flight or post-hole augers are used, the sample can be collected directly from the flights or from the borehole cuttings. The continuous flight or post-hole augers are satisfactory when a composite of the complete soil column is desired but have limited utility for sample collection as they cannot be used to sample a discrete depth.

Procedure

The following procedure is used for collecting soil samples with an auger:

Attach the auger head to an extension rod and attach the “T” handle.

Clear the area to be sampled of surface debris (e.g., twigs, rocks, litter). It may be advisable to remove a thin layer of surface soil for an area approximately six inches in radius around the sampling location.

Begin to auger, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents the accidental brushing of loose material back down the borehole when removing the auger or adding extension rods. It also facilitates refilling the hole and avoids possible contamination of the surrounding area.

After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger head.

Remove the auger tip from the extension rods and replace it with a tube sampler. Install the proper cutting tip.

Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods, as the vibrations may cause the boring walls to collapse.

Remove the tube sampler and unscrew the extension rods.

Remove the cutting tip and the core from the device.

Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern.

If VOC analysis is to be performed, transfer the sample directly from the auger head into an appropriate, labeled sample container and secure the cap tightly.

If another sample is to be collected in the same hole, but at a greater depth, reattach the auger head to the drill assembly, and follow steps 3 through 11, making sure to decontaminate the auger head and tube sampler between samples.

Fill back the hole according to State regulations (U.S. Environmental Protection Agency, 1984).

LITHO-ASSESSMENT

Lithology simply means the study of rock units. Rocks can be studied physically and chemically.

Litho-Physio Assessment

The lithology of a rock unit is a description of its physical characteristics visible on outcrop, at hand or core, and with a magnifying lens. Physical characteristics of rock include color, texture, and structural evaluation. Structural analysis proceeds through three linear stages:

Description of the structural geometry of a deformed field area (bedding attitudes, planar fabrics, linear fabrics, folds, faults, joints, and more). Description of structural geometry is the product of careful field mapping.

Kinematic analysis (movements responsible for the development of structures [translation, rotation, distortion, and dilation] and relative timing).

Dynamic analysis (interpretation of forces and stresses responsible for the deformation).

1. Geological Field Mapping

Geological mapping is a process of observations on the rock exposures, plotting them on a base map, and logically interpreting the observation towards unraveling their evolutionary history, i.e., their mode of origin, diagenesis, metamorphism, and the processes that lead to their present deposition. This also helps us to know about:

1. The age of the rock present and sometimes even the fossils and minerals they contain.
2. The distribution of rock present and the position of structures such as faults, folds, and unconformities.
3. The relationship between the older and younger rocks.
4. The mineral deposits that rock may contain.
5. The location of many physical features, such as landslides, quarries, etc.

Field Equipment and Tools

Geological mapping requires a lot of small field equipment and tools that can easily be conveyed in the field:

a) Hammer and chisels
b) Compass, clinometer
c) Camera
d) Hand lenses and tapes
e) Topographic map and field notebooks
f) Scales and protractors
g) GPS
h) Stereo net and stereoscopes.

In addition to these, pencils, erasers, and a jackknife are needed in the field.

Hammers and chisels: Geologists need a hammer and chisels. These are used to break the rock and get samples. A 1 kg hammer is the most useful one in resistive hard rock. The hammer should be fitted with a good wooden or fiberglass handle or a steel shaft. Normally, a 45 cm chisel with a 2.5 cm cutting edge is used in the field. Chipping a rock sample should be done carefully with safety glasses.

Compasses and clinometers: Geologists use a Brunton compass or a clinometer compass. This instrument detects the directions using a magnetic needle that swings freely on a pivot in a horizontal plane. One end of this needle always points to the magnetic north. The compass is normally made of brass or an alloy so that it is not susceptible to any magnetic influence. The circular dial of the compass is graduated into 360 degrees. Dip, strike, and direction are the three major measurements which can be made using the clinometer.

Hand lenses and tapes: Every geologist must have a hand lens with a magnification of between 7 and 10 times. A short roll-up steel measuring tape is always needed to measure grain sizes.

GPS: A global positioning system is needed for detecting the latitude, longitude, and elevation.

Stereonet: A pocket stereonet is most useful when mapping lineations, intersections of planes, and similar structural problems. Plunge and trend can be calculated on the spot from strike and pitch measurements made on bedding and foliation planes or from the intersection of planes. A stereonet is the geologist’s slide rule, and the structural geologist will find many uses for it in the field.

Field movement

Traversing: Traversing is a method of making observations of outcrops along a path across the location. It is a method to be repeated in roughly parallel alignment with the earlier traverse. This method helps in covering the ground in detail. The major traversing methods adopted during geological mapping are:

1. a) Cross-section traverses
2. b) Stream and ridge traverses
3. c) Road traverses

What to map: The features to be recorded are the following: rock types and contacts, shape of the rock bodies, structures including:

1. a) Folding – dip, strike, deformation, orientation of grains
2. b) Joints – attitude, size, open or closed
3. c) Faults – look for slickensides, fault gouge, breccia and their visible displacements.

Geological mapping steps:

Planning

Observation, mapping, and collecting data by examination of all geological features on the ground, Photography.

Laboratory study

Computation, Synthesis, and subsequent interpretation of data through the application of modern techniques.

Finally, preparing a report of work.

2. **Rock Sampling:**

Pearce (1996) provides a good rationale for sampling. The main goal is to collect sufficient random and fresh samples so that the main geochemical variations are adequately represented.

Litho-Geochemistry:

Litho-geochemistry is defined as the determination of the chemical composition of bedrock material with the objective of detecting distribution patterns of elements that are spatially related to mineralization. Litho-geochemistry, or rock geochemistry, is defined as the study of the chemical composition of bedrock with particular reference to the search for ore deposits. Geochemical patterns in bedrock that can be related to mineralization are referred to as primary patterns or primary dispersion, irrespective of whether the reactions causing the element distribution patterns are syngenetic or epigenetic (James, 1967).

Sample preparation:

Drying: Rock and soil samples need not be dried for days prior to crushing and grinding.

Crushing and Grinding: Large pieces of rock are broken down into smaller fragments suitable for grinding by means of a jaw crusher. Sometimes it is necessary to break very large chunks in rock trimmers prior to crushing. Jaw crushers are widely used to produce particles small enough to pass through a 2 mm sieve. Crushers whose jaws are steel-plated may contaminate samples with iron from wear on the jaws. The large amount of 2mm crushed material must be reduced to a sample of more convenient size in a manner which will yield material of the same composition as the whole. The operation called coning and quartering is often employed for this purpose. The crushed sample is placed near the center of a large sheet of glazed paper supported on a table. One corner of the paper is raised so that the sample rolls toward the opposite corner. It is important to have the sample tumble over itself in order to promote mixing. Then the other corners are raised in succession to repeat the operation. Finally, the sample is gathered near the center of the paper and is divided into quarters by means of a ruler or large spatula. Opposite quarters are removed from the paper. The operation is repeated often enough to yield a final sample of about 50 g. The coarse particles of the crushed samples must be reduced in size so that samples can be subjected to chemical methods of analysis. Particle size reductions are achieved by grinding in mortars or in ball mills. Any contamination of samples from abrasion and degradation of the grinding surfaces must be avoided as much as possible. Agate or mullite mortars are recommended for grinding by hand.

Sieving: In sieving samples, brass screens should not be used because of contamination problems. Stainless steel screens are satisfactory as long as they are not soldered. For work involving trace element analyses, non-contaminating sieves can be constructed from nylon mesh. For most chemical analyses, samples that pass through a 75-micron sieve are used.

Sample digestion: In the sample dissolution or digestion process, the sample is treated to convert insoluble components to a soluble chemical species using chemical exchange (double displacement), decomposition. The major task of sample digestion is to convert the form of the sample into one suitable for chemical analysis. The complexity of sample materials makes it necessary to choose a sample digestion method that is compatible with the specific objective of the analysis (Chao and Sanzolone, 1992). In general, the sample digestion methods can be broadly classified into five types:

i) Open vessel acid digestion

ii) Closed vessel acid digestion

iii) Microwave Digestions

iv) Partial Dissolution

v) Fusion Digestion

Very often, samples are commonly roasted at ~ 600 °C to volatilize sulfur and oxidize organic matter prior to acid attack, both of which may otherwise co-precipitate the PGE’s and also reduce Au irreversibly to its metallic form.

i. Open Vessel Digestion: This method is extremely important for routine analysis due to its flexibility in controlling digestion parameters, such as temperature, time, and the addition of reagents. However, the maximum digestion temperatures are limited by the ambient-pressure boiling point of the corresponding acid or acid mixture. Other disadvantages of open vessel digestions include the potential risk of contamination from laboratory air, the large amounts of reagents required, and the potential loss of trace elements. Therefore, open vessel acid digestion has not been considered a state-of-the-art technology in trace and ultratrace sample preparation. For the digestion of geological samples, HF in combination with other mineral acids (most commonly nitric and perchloric acids) in an open vessel is routinely used (Chao and Sanzolone, 1992; Potts and Robinson, 2003). There is also some disagreement in the literature regarding the optimum combination of acids and the role of the second acid (Langmyhr and Sveen, 1965; Tang et al., 1992). For example, Langmyhr and Sveen (1965) reported that hydrofluoric acid alone is more effective as a decomposition agent for the digestion of minerals than a mixture containing HF with another mineral acid. Tang et al. (1992) analyzed 11 Chinese geological reference materials and found no significant difference between HF/HNO3/HClO4, HF/aqua regia/HClO4, and HF/HClO4 in an open acid digestion.

ii. Closed Vessel Digestions: An important advance in acid dissolution procedures was made with the introduction of the closed acid digestion bomb popularized by Langmyhr and Paus (1968). Complete digestion of a sample is a prerequisite to achieve reproducible and accurate results in routine analysis. Digestions performed in closed vessel devices benefit from the synergic effects of temperature and pressure, where digestions reach higher temperatures because the boiling point of the reagents is raised by the pressure generated within the vessel. The principal advantages of digestion in a closed system can be summarized as follows:

This method enables the rapid digestion of refractory phases, which are not decomposed or are only partially decomposed in an open vessel.

Digestion time is significantly shortened.

Smaller reagent volumes are required.

Losses of volatile elements, such as As, B, Cr, Cd, Hg, Sb, Se, Sn, and Pb, are prevented.

Contamination is reduced by lowering reagent volumes and excluding the possible introduction of airborne particles during decomposition.

Due to these advantages, closed vessel digestions are particularly suitable for trace and ultratrace analyses, especially when the sample supply is limited.

Closed vessel acid digestion may result in the decomposition of many refractory minerals and compounds that are not decomposed or are only partially decomposed in an open vessel. To decompose silicate materials, acid mixtures such as HF/HNO3, HF/HClO4, HF/H2SO4, HF/HNO3/HCl and HF/HClO4/HNO3 have been extensively used in closed vessel digestions for multielement analysis.

iii. Microwave Digestions: Microwave digestion makes use of electromagnetic radiation with a typical frequency of 2450 MHz to generate heat. Compared with classical heating, microwave heating is many times more efficient. When irradiated by microwave energy, polar molecules and ions are energized via mechanisms of dipole rotation and ion conductance, respectively. The microwave digestion system has been used with both open and closed vessels. Moreover, it is also suitable for online digestion in continuous-flow systems (Chen *et al*. 2008). Open vessel microwave-assisted digestion is a suitable and rapid alternative to conventional hot plate digestion for mafic geological, environmental, and biological materials (Taylor *et al*. 2002). Microwave heating is also particularly applicable to closed vessel digestion because it offers the advantages of a more vigorous digestion at elevated temperatures and pressures, a reduced likelihood of contamination, and the retention of volatile elements. Many authors found that microwave digestion did not always allow the measurement of elements, such as Cr, Zr, Hf, and HREEs, especially when refractory mineral phases (e.g., zircon, chromite, rutile, corundum, and cassiterite) were present.

iv. Partial Dissolution: The purpose of partial dissolution is to save time and simplify the sample digestion procedure. The procedure for different sample types varies. To leach the total contents of elements of interest in samples, the results of a partial dissolution method should be compared with those of total dissolution with HF to evaluate the validity of the proposed method. To leach the elements of interest in one phase of the samples, the elements in the residue of the samples should not be leached. For example, 5% HNO3 was used to leach off the trace elements in the carbonate mineral phase of seep carbonates to separate the carbonate mineral phase from the residue phase (Chen *et al*. 2005). HCl, HNO3, and HClO4 are generally used when searching for ore deposits in which base metals and sulfides are of interest. Partial dissolution using HNO3 and HClO4 is useful for analyzing heavy metals in soils and sediments for environmental geochemistry studies (Lee *et al*. 2006; Luo *et al*. 2011). Partial leach procedures using aqua regia and cyanide are often used for gold exploration because a very large sample mass can be digested to measure very low concentrations of gold. Aqua regia is often used for the rapid dissolution of sulfide phases

(Church *et al*. 1987), soils, and sediments. In comparison with HF and fusion techniques, aqua regia dissolution invariably results in the retention of volatile elements (As, Hg, S, Sb, Se, etc.) in the dissolved solution (Potts and Robinson, 2003).

v. Fusion Digestion: NaOH and KOH are well-known extremely efficient fluxes for the decomposition of silicate minerals. This decomposition occurs at relatively lower temperatures (500–700 °C) and requires less time (10–30 min) than fusion with Na2CO3 and LiBO2 does. Molten alkalines are particularly corrosive, and the fusion procedures using these materials should be performed at the lowest temperature possible. The amount of NaOH and KOH used is generally at least five times the sample mass for fusion in a muffle furnace or spirit lamp. The sample powder must be well mixed with the fluxes to avoid any incomplete decomposition during the fusion; otherwise, the fluxes will not be in contact with the sample, thus resulting in partial decomposition and difficulty dissolving the alkali cake after fusion. The muffle furnace is normally heated to approximately 300°C for 30 min to remove the water in the alkali fluxes and, thus, to prevent ‘alkali creep’ over the edge of the crucible. The temperature is then increased to 650–700°C and maintained for approximately 15–30 min. The alkali cake can be rapidly dissolved with hot water and then acidified with HCl or HNO3. A silver, nickel, iron, or graphite crucible can be used for NaOH and KOH fusion.

ANALYTICAL METHODS

XRD (X-Ray Diffraction): X-Ray Diffraction analysis is a mineralogical identification method that permits semi- to full-quantitative assessment of the minerals present in a given sample and in what relative proportions they occur. The sample may be a pulverized bulk sample, a processing product, or a pure, separated mineral fraction. The method is especially suitable for the study of material containing significant small-scale variation in mineralogy (e.g., carbonates) or in mineral chemistry of component minerals or an exceptionally coarse-grained sample, inhibiting the reliability of image analysis studies of thin-sections. Reliable information can be obtained from XRD analysis of a split of a larger representative sample. The XRD method has its advantage in being a rapid technique involving only minimal sample preparation and is therefore a convenient starting point in mineral characterization procedures. It may be used to complement microscopic study of thin-sections and may be followed up by other supplementary techniques where more information is required.

XRF (X-Ray Fluorescence): X-Ray Fluorescence is one of the most common techniques used for the analysis of major and trace elements in geological samples. Analyses are performed on glass disks for major and some trace elements and pressed powder (5-10 g) pellets for most trace elements. XRF uses a primary X-ray beam to excite secondary X-rays (X-ray fluorescence), which can be detected by a crystal spectrometer for wavelength dispersive or WD-XRF, or a solid-state Si (Li) detector for energy dispersive or EDXRF (Potts, 1987; Potts et al., 1992). WD-XRF analysis has continued to evolve in the last few years primarily because of its utility in determining Ba, Rb, Sr, Y, Zr, Nb, Ti, V, Cr, and Ni with improvements in crystals and become simpler to use with end window Rh-tubes as a primary X-ray source and more sophisticated computer data reduction schemes. The precision and accuracy of WD-XRF analysis is difficult to generalize but should be on the order of 1-10%.

NAA (Neutron Activation Analysis): Neutron Activation Analysis requires irradiation of the sample (~100 mg) by a neutron flux in a nuclear reactor. The sample, standards, and flux monitor are irradiated for ~20 to 40 days, removed, and the gamma radiation emitted by the radioactive isotopes is counted using solid-state detectors. Gamma-ray spectrometry is done at a number of intervals; the first may be within hours of removal from the reactor, followed by counting after a few days and then a few weeks. The spectra produced are complicated and require relatively sophisticated peak search and peak fitting/peak area routines. Calibration is often done using an IGRM irradiated in the same batch as the unknowns. The detector geometry (planar or coaxial), detector material (pure Ge, or lithium-drifted Ge), flux rate, counting times, and sophistication of the software used all play a role in determining what elements can be measured and what their detection limits will be (Potts, 1987). The most common NAA method is strictly instrumental and is referred to as INAA. It is also possible to do separation chemistry on the sample after irradiation, radiochemical NAA (RNAA), and this method will give much better detection limits and expand the list of elements that can be determined. Research quality PGE determinations are usually done using RNAA. However, RNAA suffers from having to do chemistry on irradiated materials and is not a commonly offered package. Whereas PGE can be measured by INAA, most commercial labs offer this only as a choice if combined with fire assay (FA) concentration. INAA is a common choice amongst geochemists because of its relatively low cost, ease of sample preparation, and wide selection of elements. For geochemists, INAA is attractive because it gives the LFSE Th, the HFSE Ta and Hf, plus some of the REE. INAA REE patterns are usually easily identified by the common absence of Dy and Er, and sometimes they also lack Gd. Precision and accuracy in INAA are generally on the order of 2-10% (Potts, 1987).

ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometry): Inductively Coupled Plasma – Atomic Emission Spectrometry is becoming the technique of choice in commercial labs and in many academic institutions. The technique makes use of a high-temperature inductively coupled plasma and with simultaneous detectors can produce high-quality major and trace element data in a very short period of time (20 to 60 elements in 2-3 minutes, Potts, 1987). The spectra emitted in ICP-AES are not simple but are becoming much better understood and are free of the degree of chemical interferences found in atomic absorption spectrometry (AAS). The range of elements, accuracy, and precision of ICP-AES are similar to that found using XRF; however, unlike trace elements analysis using XRF, the samples must be dissolved before analysis. The need to dissolve the sample increases the cost, preparation time, possibilities of contamination, and incomplete dissolution and solution stability/concentration problems. With the addition of a chemical separation stage, the REE elements can be determined using ICP-AES, with an accuracy and precision comparable to that of INAA or better (Potts, 1987). In general, for labs which are used to doing a lot of wet chemistry, ICP-AES has replaced AAS and is an alternative to INAA and XRF.

ICP-MS (Inductively Coupled Plasma – Mass Spectrometry): Inductively Coupled Plasma – Mass Spectrometry couples the high-temperature plasma of the ICP to the rapid scanning, high sensitivity, and good resolution capabilities of a quadrupole mass spectrometer. The technique can produce high-quality data on a wide range of elements, using a variety of sample weights (0.1 to 100 mg). Isotope ratios can be measured using ICP-MS, with sufficient precision for certain U-Pb dating (and other isotope applications) and allow for isotope dilution as a method to determine element concentration. ICP-MS is becoming the method of choice in many geochemical facilities, replacing INAA, RNAA, and XRF for trace element determinations. ICP-MS is not without difficulties, including problems with matrix, drift, interferences, memory, and background; problem areas that are often interrelated. Nonetheless, this technique has proven itself capable of matching isotope dilution thermal ionization mass spectrometry and spark source mass spectrometry in terms of accuracy and precision at low trace element concentrations (Jenner *et al*. 1990; Jochum *et al*. 2000).

These analytical methods are summarized in Table 1

Table I: Summary of Analytical Methods

S/NO	METHODS	APPLICATION	ADVANTAGES	LIMITATION
1.	AAS	For elemental analysis of solutions	It is less sophisticated but provides quality results and fast analysis of element	Low sensitivity to non metals, analyze individual elements
2.	ICP MS	Multi element analysis	Allows rapid determination of many elements in a short period of time, high sensitivity and low detection limit	Elemental interferences Difficult to analyze non-volatile samples

3.	XRF	Elemental analysis (major and trace elements) for solids and non-volatile liquids	High sensitivity and minimum sample preparation	Not sensitive to elements with atomic mass < Na, and most suitable for major element analysis
4.	XRD	Mineralogy of solids	Can distinguish polymorphs, isomers and conformers, less expensive and used for identification of minerals	Detection and sensitivity depend on crystallite size
5.	NAA	Elemental analysis of major and trace elements for solid and liquid	Very high sensitivity for many elements	Highly sensitive.

DATA ANALYSIS

There are various approaches to detecting geochemical patterns that can be spatially related to mineralization. Recent developments in advanced multivariate analytics, geospatial analysis, and mapping provide an effective framework to analyze and interpret geochemical datasets. Geochemical and geological processes can often be recognized through the use of data discovery procedures such as principal component analysis. Classification and predictive procedures can be used to confirm lithological variability, alteration, and mineralization. The data characterization step is a prerequisite for successful data cleaning and transformation before approaching multivariate statistical analysis (Reimann et al., 2002). During the different analysis steps, Geographic Information Systems (GIS) in combination with statistical, geostatistical, and geochemical methods are commonly used (Zhang & Selinus, 1998; Grunsky & Smee, 1999; Lin, 2002; Romic & Romic, 2002).

However, exploratory data analysis (EDA) tools are currently being used for geochemical data analyses. EDA uses techniques from statistics and graphics. Many exploratory methods emphasize graphical views of the data that highlight particular features. Major advantages of EDA are the straightforward application of its techniques and the easily interpretable results.

Measurement of Geochemical Data: Major elements are commonly expressed as weight % oxides. Trace elements are expressed as parts per million (ppm). They should be converted to moles and then evaluated.

1. **Statistical Data Analysis:**

The most commonly used multivariate techniques for studying geochemistry are:

Principal component analysis (PCA) to identify the predominant element associations (or geochemical processes) in multi-element data.

Independent Components

Multi-dimensional scaling

Cluster analysis: sample associations can be detected with cluster analysis.

Factor analysis: to identify the predominant element associations (or geochemical processes) in multi-element data.

Mahalanobis Distance Plots ($\chi 2$ plots): multivariate equivalent of quantile-quantile plot.

Regression analysis: inter-element and inter-sample relationships can be studied with regression analysis.

Empirical Indices

2. **Geostatistical Data Analysis**:

This involves spatial processes using an image analysis system. Spatial forms of multivariate statistical analysis are used to examine data from a spatial perspective, exploring spatial patterns and relationships (Äyräs & Kashulina, 2000). This can be achieved with spatial evaluation bubble plots and interpolated images. Anomalies can be recognized using fractals.

3. **Geochemical Data Analysis:**

There is no substitute for spending time evaluating the data using a wide variety of procedures so that associations and structures in the data can be identified.

Examine each element using histograms, box and whisker plots, Q-Q plots, a scatter plot matrix, and summary tables.

Produce maps of elements showing the range of values using bubble or symbol plots. Interpolated images can be used where appropriate.

If measures of association are required (i.e., correlation, covariance), consider the application of log-ratio transformations (e.g., log-centered, isometric log-ratio).

Examine scatter and quantile-quantile plots for the presence of multiple populations.

Create a scatter plot matrix of the transformed (log-centered ratios, isometric log-ratios) data. Look for trends and/or associations.

The application of dimension-reducing techniques, such as principal components analysis, can identify patterns and trends in the data. Other methods, such as non-linear mapping, multi-dimensional scaling, and self-organizing maps, may help discover structure in the data.

Methods such as cluster analysis can help to isolate groups of observations with similar characteristics and a typical observation. Specific groups of interest can often be isolated using these methods. Maps of the locations of the groups can help to examine the spatial continuity of the groups.

The use of Mahalanobis distance plots (X2) applied to transformed data may assist in isolating outliers based on a selected number of elements of interest.

The calculation of specifically tailored empirical indices can be useful in areas where multi-element associations are well understood. The indices are based on a linear combination of pathfinder elements with coefficients that are selected for each area and commodity being sought. Observations with high indices can be investigated for mineralization potential (Grunsky, 2017).

REFERENCES

1. Adepoju, M. O.; Adekoya, J. A. and Awoniran, D. R. (2019). Exploration for ferrous metals using geochemical soil survey in Dagbala-Atte district, Southwestern Nigeria. International Advanced Research Journal in Science, Engineering and Technology 6 (3): (pp100-111).

2. Adepoju, M. O., Okonkwo, C. T. and Bolarinwa, A. T. (2021). Pedogeochemical survey for uranium mineralization in parts of Igarra schist belt, southwestern Nigeria. Ife Journal of Science vol. 23, no. 2 (pp 191-204).
3. Adesiyan A.; Adekoya A.; Akinlua A. and Torto N. (2014). Statistical Studies of Soil Geochemical Data from Gbongan-Odeyinka Area, Southwestern Nigeria. Geoinfor Geostat 2014; (pp 2-11).
4. Ajayi T.R. (1981). Statistical Analysis of Stream Sediment Data from the Ife-Ilesha Area of Southwest Nigeria Journal of Geochemical Exploration 1981;15: (pp 539-548).
5. Alao-Daniel, A. B, Adetunji, A, Opuwari, M. A. and Eruteya, O. E. (2023). Integrated Multi-Elemental Soil Geochemical Survey as a Tool in Geological Mapping in the Tropics: A Case Study of Songbe Area of Osun State, West Africa. DOI:10.7537/marsnsj210423.05.
6. Äyräs, M. & Kashulina, G. (2000). Regional patterns in the central part of the Barents region (heavy metals (Co, Cr, Cu, Fe, Ni, Pb, V and Zn) and sulphur as indicators of airborne pollution. Journal of Geochemical Exploration, 68. (pp126-144).
7. Boyle RW and Jonasson IR (1973). The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. Journal of Geochemical Exploration 2: (pp 251–296).
8. Brandy, N. C. and Weil, R. R. (1996). The nature and properties of soils. Prentice hall inc., new Jersey.
9. Cameron EM, Hamilton SM, Leybourne MI, Hall GEM, and McClenaghan MB (2004). Finding deeply buried deposits using geochemistry. Geochemistry: Exploration, Environment, Analysis 4. (pp7–32).
10. Chao TT and Sanzolone RF (1992). Decomposition techniques. Journal of Geochemical Exploration 44: (pp 65–106).
11. Chen LG, Song DQ, Tian Y, Ding L, Yu AM, and Zhang HQ (2008). Application of on-line microwave sample-preparation techniques. TrAC Trends in Analytical Chemistry 27: (pp 151–159).
12. Chen D. F.; Huang Y. Y.; Yuan X. L. and Cathles L. M. (2005). Seep carbonates and preserved methane oxidizing archaea and sulfate reducing bacteria fossils suggest recent gas venting on the seafloor in the Northeastern South China Sea. Marine and Petroleum Geology 22: (pp 613–621).
13. Church, S. E, Mosier, E.L, and Motooka, J.M. (1987). Mineralogical basis for the interpretation of multielement (ICP-AES), oxalic-acid, and aqua regia partial digestions of stream sediments for reconnaissance exploration geochemistry. Journal of Geochemical Exploration 29: (pp 207–233).
14. David Cohen and Rob Bowell (2013). Exploration Geochemistry Research Gate Article . DOI: 10.1016/B978-0-08-095975-7.01127-X. (pp 623 – 649).
15. Govett, G.J.S., (1973). Differential secondary dispersion in transported soils and post-mineralization rocks: An electrochemical interpretation. In: Jones MJ (ed.). Geochemical Exploration 1972,. London: Institution of Mining and Metallurgy (pp. 81–91).
16. Grunsky, E.C. & Smee, B.W. (1999). The differentiation of soil types and mineralization from multi-element geochemistry using multi variate methods and digital topography. Journal of Geochemical Exploration 67: (pp287-299).
17. Grunsky, E.C., Caritat, P.de & Mueller, U.A. .2017). Using surface regolith geochemistry to map the major crustal blocks of the Australian continent. Gondwana Research, 46, https://doi.org/10.1016/j.gr.2017.02.011 (pp227–239).
18. James, C. H. (1967). The use of the terms “primary” and “secondary” dispersion in geochemical prospecting; Econ. Geo., v. 62, (pp 997-999).
19. Jenner G. A.; Longerich H. P.; Jackson S. E. and Fryer B. J. (1990). ICP-MS – A powerful tool for high-precision trace-element analysis in earth sciences: Evidence from analysis of selected U.S.G.S. reference samples. Chemical Geology 83: (pp133–148).
20. Jochum K.P.; Dingwell D. B.; Rocholl A. *et al*. (2000) The preparation and preliminary characterisation of eight geological MPI-DING reference glasses for in-situ microanalysis. Geostandards Newsletter 24: (pp 87–133).
21. Juvonen R, Kallio E, and Lakomaa T (1994). Determination of precious metals in rocks by inductively coupled plasma mass spectrometry using nickel sulfide concentration. Comparison with other pre-treatment methods. Analyst 119: (pp 617–621).

22. Juvonen R, Lakomaa T, and Soikkeli L (2002). Determination of gold and the platinum group elements in geological samples by ICP-MS after nickel sulphide fire assay: Difficulties encountered with different types of geological samples. Talanta 58: (pp 595–603).
23. Large, R. R; Allen, R. L, Blake MD, and Herrmann, W. (2001). Hydrothermal alteration and volatile element halos for the Rosebery K Lens volcanic hosted massive sulfide deposit, Western Tasmania. Economic Geology 96: (pp 1055–1072).
24. Langmyhr, F. J. and Steven, S. (1965). Decomposability in hydrofluoric acid of the main and some minor and trace minerals of silicate rocks. Analytica Chimica Acta 32: (pp 1–7).
25. Langmyhr, F. J. and Kringstad, K. (1966). An investigation of the composition of the precipitates formed by the decomposition of silicate rocks in 38–40% hydrofluoric acid. Analytica Chimica Acta 35: (pp 131–135).
26. Langmyhr, F. J. (1967). The removal of hydrofluoric acid by evaporation in the presence of sulfuric or perchloric acids. Analytica Chimica Acta 39: (pp 516–518).
27. Langmyhr, F. J. and Paus, P. E. (1968). The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part I. The analysis of silicate rocks. Analytica Chimica Acta 43: (pp397–408).
28. Lee CS, Li XD, Shi WZ, Cheung SC, and Thornton I (2006). Metal contamination in urban, suburban, and country park soils of Hong Kong: A study based on GIS and multivariate statistics. Science of the Total Environment 356: (pp 45–61).
29. Lin, Y.-P. (2002). Multivariate geostatistical methods to identify and map spatial variations of soil heavy metals. Environmental Geology, 42: (pp 1-10).
30. Luo XS, Yu S, and Li XD (2011). Distribution, availability, and sources of trace metals in different particle size fractions of urban soils in Hong Kong: Implications forassessing the risk to human health. Environmental Pollution 159: (pp 1317–1326).
31. Omorinoye, O.A.1 & Adekeye , J.I.D., (2013). Soil Geochemical Survey of Eruku and Environs. Journal of Environment and Earth Science ISSN 2225-0948 (Online) Vol. 3, No.7 (pp 102-113).
32. Pearce, J.A., (1987). An expert system for the tectonic characterization of ancient volcanic rocks: Journal of Volcanological and Geothermal Research, v. 32. (pp51-65).
33. Potts P. J. (1987). A Handbook of Silicate Rock Analysis. Glasgow: Blackie, (pp 1–622).
34. Potts P. J; Gowing C. J. B. and Govindaraju K. (1992) Preparation, homogeneity evaluation and cooperative study of two new chromitite reference samples CHR-Ptþ and CHRBkg. Geostandards Newsletter 16: (pp 81–108).
35. Reimann, C. & Filzmoser, P. (2000). Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and Environmental Geology, 39: (pp 1001-1014).
36. Rose A. W.; Hawkes H. E. and Webb J. S. (1991). Geochemistry in Mineral Exploration. 3rd ed. London: Academic Press; 1991. p. 711.
37. Potts PJ and Robinson P (2003). Sample preparation of geological samples, soils and sediments. In: Mester Z and Sturgeon R (eds.) Sample Preparation for Trace Element Analysis. The Netherlands: Elsevier. pp. 723–763).
38. Romic, M. & Romic, D. (2002). Heavy metals distribution in agricultural top soils in urban area. Environmental Geology, 43(7): (pp 795-805).
39. Tang Y. Q.; Jarvis K. E. and Williams J. G. (1992). Determination of trace elements in 11 Chinese geological reference materials by ICP-MS. Geostandards Newsletter 16: pp 61–70.
40. Taylor VF, Toms A, and Longerich HP (2002). Acid digestion of geological and environmental samples using open-vessel focused microwave digestion. Analytical and Bioanalytical Chemistry 372: (pp360–365).
41. Turnbull, R. E., A.P. Martin, M.S. Rattenbury, A.B. Christie (2015). Regional soil geochemical baseline data for mineral exploration, southern New Zealand. Researchgate.net/publication/283422640.
42. U.S. Environmental Protection Agency, (1984). Characterization of Hazardous Waste Sites – A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076.

43. Zhang, C. & Selinus, O. (1998). Statistics and GIS in environmental geochemistry – some problems and solutions. Journal of Geochemical Exploration, 64: (pp 339-354).