THE FACTORS AFFECTING THE INTERPRETATION OF GEOCHEMICAL SURVEYS IN MINERAL EXPLORATION

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CONTENTS

1.0.0. INTRODUCTION.

> Boob's Law (from Murphy's Law):
> "You always find something the last
> place you look." (Bloch, 1980).

Exploration geochemistry is an indirect method of detecting mineral deposits by measuring the abundance and distribution of ore elements and elements closely associated with ore in natural materials at or near the earth's surface. The method relies on the assumption that a mineral deposit is reflected by unusual element abundances or distribution patterns (geochemical halos), and that these indications of mineralization can be detected by geochemical surveys involving the collection and analysis of natural materials.

The interpretation of geochemical surveys in mineral exploration involves:

1) The use of geological and statistical inference, based on a knowledge of the normal behaviour and distribution of indicator elements in the exploration area, to recognize apparent geochemical anomalies in field and analytical data and to predict the type of geochemical halo reflected by the anomalies.

11) The use of geological inference, based on a knowledge of the characteristics of geochemical halos and their relationship to mineral deposits, to predict the presence and probable location of an ore body.

The interpretation process is, however, complicated by the absence of a simple universal formula that relates the abundance and distribution of elements in natural materials to the presence or absence of a mineral deposit. The interpretation of a geochemical survey must, thus, be based on an empirical approach which avaluates each survey as an individual problem.

The objective of this dissertation is to illustrate the factors affecting the "nuts and bolts" approach to the interpretation of geochemical surveys in mineral exploration. The discussion is aimed at providing field geologists responsible for the planning and execution of geochemical surveys with some basic guidelines for interpreting the surveys. I hope that the contents of this dissertation will help field geologists to "look in the last place first".

2.0.0. GEOLOGICAL FACTORS.

> Grossman's misquote of H.L. Mencken:
> "Complex problems have simple, easy to understand, wrong answers." (Bloch, 1980)

2.1.0. The Distribution of Elements in the Lithosphere.

2.1.1. The primary geochemical environment.

The earth's crust consists of three geospheres with different compositional and physical characteristics viz. the lithosphere, hydrosphere and atmosphere (Beus and Grigorian, 1977). The lithosphere consists of magmatic, metamorphic and sedimentary rocks and is the main object of study in the search for mineral deposits. Exploration is largely confined to the near surface portion of the continental lithospere which can be divided into two environments for the purposes of geochemical exploration viz. the surficial environment (discussed in section 3.0.0.) and the primary geochemical environment.

The primary environment, as used in this dissertation, refers to the bedrock below the level of weathering and excludes unconsolidated surficial overburden (e.g. recent glacial till, alluvial sediments etc.). Primary dispersion patterns refer to the geochemical characteristics of unweathered rocks including the geochemical halos related to mineral deposits. The processes responsible for primary dispersion patterns include the processes of magmatism, hydrothermal activity and metamorphism as well as the shallow processes of volcanism, sedimentation and diagenesis. Geochemical patterns in sedimentary rocks formed by surficial processes are, thus, included in the definition of primary dispersion patterns as proposed by James (1967).

2.1.2. The abundance of elements in the lithosphere.

The understanding and interpretation of geochemical dispersion in geological environments requires a basic classification of elements according to their crustal abundances. Vernadskii (in Beus and Grigorian, 1977) classified the elements into categories based on a 10-fold symmetry of their abundance in continental lithosphere (Table 2.1.). The elements in the "decades" can be divided into major (or rock-forming) elements ($>$ 1%), minor elements (0,1% - 1%) and trace elements ($<$ 0,1%). The decades emphasize the relatively small average amounts of most of the important ore-forming elements which occur in the major grouping of 39 elements having crustal abundances of 1 p.p.m. to 100 p.p.m.

Table 2.1 Distribution of the average contents of 82 elements in the continental lithosphere based on Vernadskii's "decades". After Beus and Grigorian (1977).

Decade	Average content in decade (in weight %)*	Number of elements	Element
I	>10	2	O, Si
II	10^{0} - 10^{1}	6	Al, Fe, Ca, Mg, Na, K
III	10^{-1} - 10^{0}	4	Ti, P, H, C
IV	10^{-2} - 10^{-1}	9	Mn, S, F, Ba, Sr, V, Cr, Zr, Cl
V	10^{-3} - 10^{-2}	14	Ni, Rb, Zn, Cu, Co, Ce, Y, La, Nd, Sc, N, Li, Ga, Nb
VI	10^{-4} - 10^{-3}	25	Pb, B, Th, Sm, Gd, Pr, Dy, Er, Yb, Hf, Br, Cs, Sn, As, Be, Ar, U, Ge, Mo, Ho, He, Eu, Tb, W, Ta
VII	10^{-5} - 10^{-4}	8	Lu, Tl, I, In, Sb, Tm, Gd, Se
VIII	10^{-6} - 10^{-5}	5	Ag, Hg, Bi, Ne, Pt
IX	10^{-7} - 10^{-6}	4	Pd, Te, Au, Os
X	10^{-8} - 10^{-7}	3	Re, Ir, Kr
XI	10^{-9} - 10^{-8}	1	Xe
XII	10^{-10} - 10^{-9}	1	Ra

The elements are, however, inhomogeneously distributed in the primary environment. Rocks of the lithosphere which belong to the same specific rock type are, as a rule, characterized by a very similar composition of their major components, but the content of trace elements in each rock type is likely to vary appreciably.

Published tables of the "average" contents of major, minor and trace elements in various rock types (e.g. Beus and Grigorian, 1977, pp 7 to 10; and Levinson, 1974, pp 43) can be used as a general guide to expected element concentrations. The interpretation of geochemical surveys should, however, be based on a table giving the expected ranges of background concentrations of elements in the various rock types present in the exploration area. The tables should be compiled for specific regions of interest from the analysis of rock samples, from published information and from previous experience. They should be used to define diagnostic elements for various lithological units and the expected background concentrations of target and pathfinder elements being used in the exploration programme.

The imbalanced distribution of elements in rocks is the basis of geochemical exploration. The variability occurs on a number of scales:

a) The chemical composition, and particularly the trace element content, of groups of rocks may be characterized by regional geochemical similarities. The regional characteristics (e.g. higher than average contents of particular elements in all rock types) can be used to define geochemical provinces.

b) Sedimentary units, plutons or volcanic horizons within a region may show geochemical specialization in relation to similar rock types in the area. The trace element content of the specialized rock types (e.g. an ultrabasic volcanic unit with above average nickel and sulphur contents) can indicate a genetic relationship of particular types of mineral deposits (e.g. magmatic nickel sulphide deposits). The geochemical specialization of particular rock types and the variation between different rock types affect the geochemical background values of an area.

c) The normal background values of various rock types, particularly the trace element contents, tend to deviate in the vicinity of mineral deposits. The variations are related to the genesis of the mineral deposits. Dispersion halos may be syngenetic and epigenetic in relation to the rocks surrounding the mineral deposit, depending on the genetic relationships between the rock units and the mineral deposit.

d) The variations in any of the above categories may be due to the presence of specific minerals or to variations in the normal composition of rock forming minerals.

The characteristics of primary geochemical dispersion patterns are dependent on the chemical behaviour of the elements involved and on the processes active in various geological environments.

2.1.3. The chemical behaviour of the elements.

The interpretation of the distribution of elements in the primary and secondary environments requires a scheme of grouping the elements such that their properties can be more easily related to their chemical behaviour. The periodic table, based on the intricate relationships between the electronic structures of elements is a convenient basic classification for geochemical purposes. A large number of chemical and physical properties of the elements vary periodically with atomic number (Fig. 2.1). Properties such as ionization energy, electron affinity, possible oxidation

TABLE OF PERIODIC PROPERTIES OF THE ELEMENTS

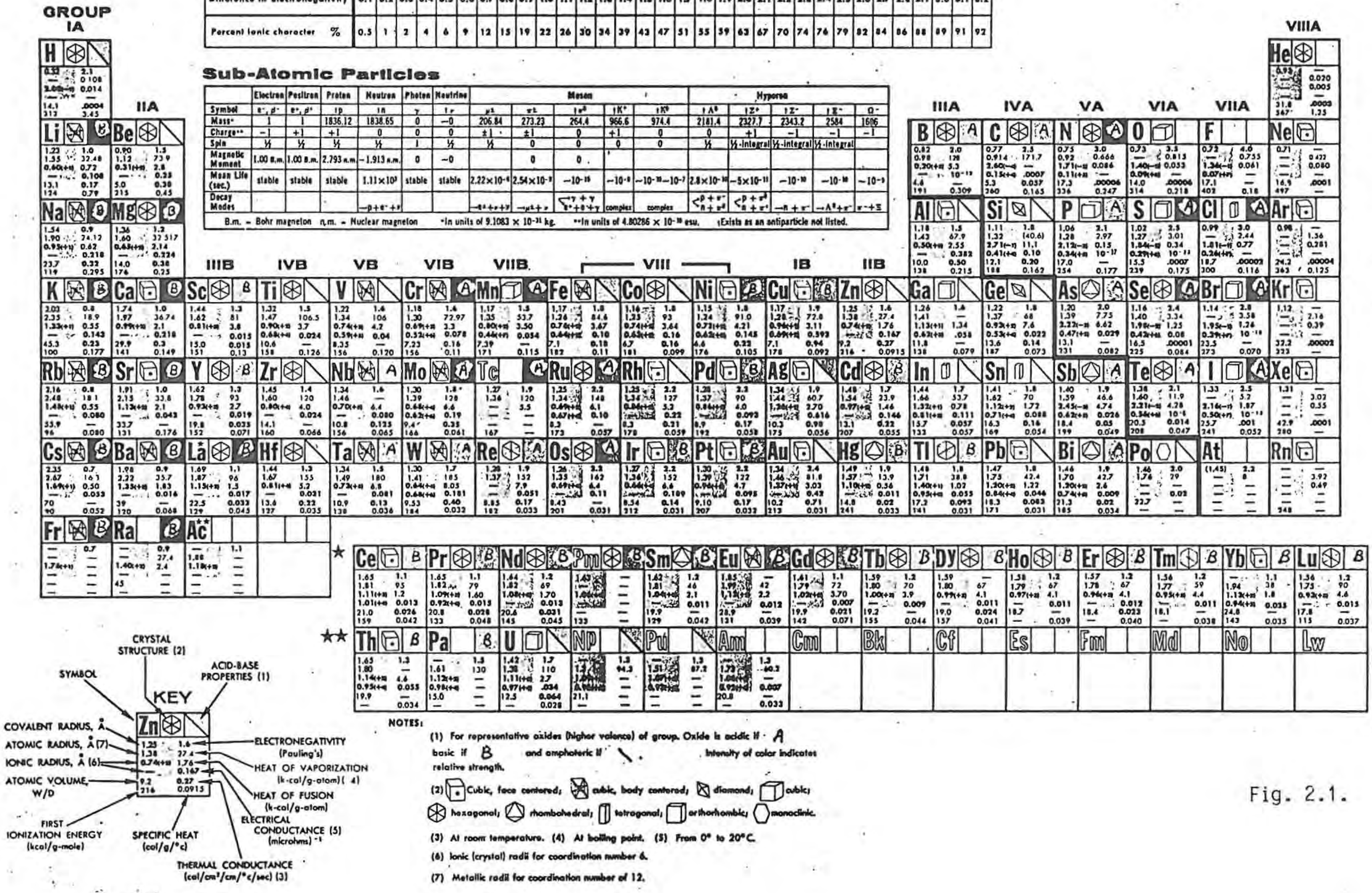
Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Sub-Atomic Particles

	Electron	Positron	Proton	Neutron	Photon	Neutrino	Meson					Hyperon				
Symbol	e^-, β^-	e^+, β^+	†p	†n	γ	†ν	$\mu^\pm$	$\pi^\pm$	†π^0	†K^+	†K^0	†Λ^0	†Σ^+	†Σ^-	†Ξ^-	Ω^-
Mass*	1	1	1836.12	1838.65	0	~0	206.84	273.23	264.4	966.6	974.4	2181.4	2327.7	2343.2	2584	1606
Charge**	−1	+1	+1	0	0	0	±1	±1	0	+1	0	0	+1	−1	−1	−1
Spin	½	½	½	½	1	½	½	0	0	0	0	½	½-integral	½-integral	½-integral	
Magnetic Moment	1.00 B.m.	1.00 B.m.	2.793 n.m.	−1.913 n.m.	0	~0		0	0							
Mean Life (sec.)	stable	stable	stable	1.11×10^3	stable	stable	2.22×10^{-6}	2.54×10^{-8}	$\sim10^{-16}$	$\sim10^{-8}$	$\sim10^{-10}-10^{-7}$	2.8×10^{-10}	$\sim5\times10^{-11}$	$\sim10^{-10}$	$\sim10^{-10}$	$\sim10^{-9}$
Decay Modes				$\rightarrow p+e^-+\bar{\nu}$			$\rightarrow e^\pm+\nu+\bar{\nu}$	$\rightarrow \mu^\pm+\nu$	$\gamma+\gamma$ $e^++e^-+\gamma$	complex	complex	$p+\pi^-$ $n+\pi^0$	$p+\pi^0$ $n+\pi^+$	$\rightarrow n+\pi^-$	$\rightarrow \Lambda^0+\pi^-$	$\pi^-+\Xi$

B.m. = Bohr magneton n.m. = Nuclear magneton *In units of 9.1083×10^{-31} kg. **In units of 4.80286×10^{-10} esu. †Exists as an antiparticle not listed.



NOTES:

(1) For representative oxides (higher valence) of group. Oxide is acidic if A basic if B and amphoteric if ╲. Intensity of color indicates relative strength.

(2) Cubic, face centered; cubic, body centered; diamond; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.

(3) At room temperature. (4) At boiling point. (5) From 0° to 20°C.

(6) Ionic (crystal) radii for coordination number 6.

(7) Metallic radii for coordination number of 12.

Fig. 2.1.

states and atomic size can be used to predict the chemical behaviour of the elements and their mobility in various geological environments. The periodic table also groups the elements into blocks which have similar properties viz. the active metals, transition metals, semi-metals, active non-metals and inert gases. The groups of elements simplify the interpretation of element behaviour in geological environments as elements in each group have similar chemical characteristics.

Predictions about the geological behaviour of the elements based on the periodic laws are generally less successful than predictions of chemical behaviour. The periodic laws predict, for example, that molybdenum and chromium should be closely associated, but these elements do not occur together in nature. Understanding the distribution of elements in geological environments must, thus, be based on more detailed studies of the behaviour of elements and the factors affecting element mobility in deep-seated and surficial environments. Anderson (1978) reviewed the behaviour of the elements Ni, Co, Cu, Pb, Zn, Au, Ag, Mo, Sn, W and U in the magmatic, hydrothermal, sedimentary and weathering environments. The review shows the importance of considering aspects of crystal chemistry (e.g. crystal field theory) as well as the chemistry and geochemistry of elements in order to understand and predict their behaviour in various geological environments and during ore forming processes. The factors discussed by Anderson have an important bearing on the interpretation of geochemical surveys of all types and the reader is referred to Anderson's study for details of the geological behaviour of the elements concerned. The dissertation also serves to illustrate the type of information required to predict and interpret the distribution of elements in the lithosphere.

2.1.4. Element associations and the modes of occurrence of elements in the lithosphere.

The interpretation of geochemical surveys is essentially a process of geological inference based on the distribution and concentration of selected elements in a particular geological environment. The recognition of element associations is a fundamental aspect of geological inference. Joyce (1976) summarizes the importance of natural associations in geology as follows:

"No element, mineral, nor rock type should ever be considered in isolation. The mention of any element, mineral or rock type should con-

Table 2.2 Geochemical classification of elements in the Earth's crust. After Beus and Grigorian (1977).

Type	Major (> 1%)	Minor (0.1-1.0%)	Trace elements (< 0.1%)	
			Mineral-forming	Dispersed
I. Oxyphile				
a. Lithophile	O, Si, Al, Fe, Mg, Ca, Na, K	Mn, Ti, P, (C)	Li, Be, B, F, Sr, Ba, Y and rare earth elements, Zr, Nb, Ta, Sn, Cs, W, Th, U	Ga, Ge, Rb, Hf, Sc, Ra, (Tl)
b. Siderophile	Fe	—	V, Cr, Co, Ni	—
II. Chalcophile	—	—	S, Cu, Zn, As, Se, Mo, Ag, Sb, Te, Hg, Pb, Bi	Cd, In, Re, Tl, (Ga), (Ge)
III. Noble	—	—	Pd, Os, Ir, Pt, Au	Rh, Ru
IV. Hydrophile	(O)	H	Cl, Br, I, (S)	
V. Atmophile	(O)	C	He, N, Ne, Ar, Xe, Rn	

Table 2.3. Summary of the implications of Goldschmidts' classification of the elements (modified by Beus and Grigorian, Table 2.2.)

1)	Oxyphile Group:	The elements show a marked affinity for oxygen in the lithosphere. The group includes most of the major and minor elements.
1a)	Lithophile Sub-group:	The elements commonly occur as silicates and form the chemical basis of crustal material.
1b)	Siderophile Sub-group:	The elements tend to accumulate in association with iron in the lithosphere.
11)	Sulphophile (Chalcophile) Group:	The group includes chemical elements with a marked affinity for sulphur, which usually occur as sulphides and have a tendency to accumulate together with sulphur in sulphide deposits.
111)	Noble Element Group:	The elements generally occur in nature as native metals.
1V)	Hydrophile Group:	The group consists of the typical elements of the hydrosphere which mostly constitute the anionic part of chemical compounds in aqueous solutions.
V)	Atmophile Group:	The group includes elements of the atmosphere and gaseous components of the lithosphere.
V1)	Biophile Group:	The principal constituents of living matter are O, C and H with minor amounts of Cu, K, N, Mg, P, S, Cl, Na and Fe. The rest of the elements occur in trace amounts in the biosphere.

jure up an immediate association with other related elements, minerals, rocks, processes, tectonic settings, etc."

The observed associations of the elements in nature prompted Goldschmidt to develop a classification of the elements on the basis of the stability of the compounds they form with other elements. Beus and Grigorian (1977) have modified Goldschmidt's classification in order to represent the element associations commonly found in the crustal lithosphere, which is of most interest to exploration geochemistry (Table 2.2.). The classification emphasizes the marked affinity for oxygen of a large proportion of the chemical elements in the lithosphere. The implications of Goldschmidts' classification are summarized in Table 2.3.

The mode of occurrence of chemical elements in rocks is a fundamental factor for the understanding of element associations. Beus and Grigorian, (1977, summarized by Levinson, 1980, p 632) distinguish three modes of occurrence of elements in the lithosphere:

a) Elements present in rocks as independent structural components of minerals.

The major elements (Vernadskii's first two decades, Table 2.1.) occur as independent components in the stoichometric formula of minerals, such as silicates, and make up the bulk of the lithosphere. The minor elements (e.g. Ti and P) also tend to be concentrated in rocks as their own minerals. The mineral-forming trace elements (e.g. Se, Te, Tu, Be etc., in Table 2.2), are capable of forming numerous minerals, even though their average contents in the lithosphere are very low. The principal minerals formed by minor and trace elements in rocks of the lithosphere are listed in Table 2.4.

b) The isomorphous form of element occurrence.

The mineral forming trace elements commonly occur as disseminated admixtures within the crystal structures of other minerals and as trace mineral inclusions in the rock foming minerals. The dispersed trace elements (Table 2.2) very rarely form their own minerals and tend to occur in the mineral structures of closely associated more abundant elements (e.g. Ga-Al, Rb-K). The substitution of trace elements for more abundant elements in the crystal lattic is dependent on similarities in ionic size and valency, as well as the type of chemical bond formed

Table 2.4 Principal minerals formed by minor and trace elements in rocks of the lithosphere. From Beus and Grigorian (1977).

Element	Granites and granodiorites	Intermediate rocks	Basic rocks	Alkaline rocks	Ultrabasic rocks
Titanium	ilmenite, sphene	ilmenite sphene	ilmenite, titanomagnetite	ilmenorutile, sphene, complex titanium silicates	—
Phosphorus	apatite, monazite	apatite	apatite	apatite	—
Sulfur	sulfides of iron, copper, lead, zinc, etc.				
Boron	tourmaline	—	—	—	—
Zirconium	zircon	zircon	—	zircon, complex zirconium silicates	—
Lithium	lithium micas, amblygonite, spodumene (in metasomatically altered granites)	—	—	—	—
Beryllium	beryl, bertrandite, phenacite, chrysoberyl (in metasomatically altered granites)	—	—	—	—
Fluorine	fluorite, topaz	—	—	villiaumite, fluorite	—
Chromium	—	—	chromite	—	chromite
Manganese	secondary oxides	secondary oxides	secondary oxides	secondary oxides	secondary oxides
Copper, zinc, lead, nickel	sulfides	sulfides	sulfides	sulfides	sulfides
Arsenic	arsenopyrite	arsenopyrite	arsenopyrite	—	—
Molybdenum	molybdenite	—	—	molybdenite	—
Tin	cassiterite	—	—	—	—
Rare-earth elements	monazite, allanite, xenotime, rare-earth niobates	—	—	loparite, complex silicates	—
Niobium and tantalum	Columbite-tantalite, pyrochlore-microlite, rare-earth tantalo-niobates (in metasomatically altered granites)	—	—	loparite	—
Thorium	monazite, thorite	—	—	thorite	—
Uranium	uranium oxides, phosphates, etc.	—	—	—	—

Table 2.5 Selected elements found in small amounts in common rock-forming minerals of igneous rocks, and relative stability of the minerals.

Mineral	*X%*	*0.X%*	*0.0X%*	*0.00X% and less*	*Stability*
Olivine	—	Ni, Mn	Ca, Al, Cr, Ti, P, Co	Zn, V, Cu, Sc	
Amphibole	—	Ti, F, K, Mn, Cl, Rb	Zn, Cr, V, Sr, Ni	Ba, Cu, P, Co, Ga, Pb, Li, B	
Pyroxene	—	Ti, Na, Mn, K	Cr, V, Ni, Cl, Sr	P, Cu, Co, Zn, Li, Rb, Ba	Easily Weathered
Biotite	Ti, F	Ca, Na, Ba, Mn, Rb	Cl, Zn, V, Cr, Li, Ni	Cu, Sn, Sr, Co, P, Pb, Ga	
Plagioclase	K	Sr	Ba, Rb, Ti, Mn	P, Ga, V, Zn, Ni, Pb, Cu, Li	
Epidote	RE	Mn, Ti	Th, Sn	V, Nb, Zn, Be, U	
Sphene	—	RE, Nb, Sn, Sr	Mn, Ta, V, Cr	Ba	
Apatite	—	Sr, RE, Mn	U, Pb	As, Cr, V	
Garnet	Mn, Cr	Ti, RE	Ga	—	Moderately Stable
Feldspar (potash)	Na	Ca, Ba, Sr	Rb, Ti	Pb, Ga, V, Zn, Ni, Cu, Li	
Muscovite	—	Ti, Na, Fe, Ba, Rb, Li	Cr, Mn, V, Cs, Ga	Zn, Sn, Cu, B, Nb	
Tourmaline	—	Ti, Li, Mn	Cr, Ga, Sn, Cu, V	Rb	
Magnetite	Ti, Al, Cr	Mn, V	Zn, Cu, Sn, Ni	Co, Pb, Mo	
Zircon	Hf	RE, Th	Ti, Mn, P	Be, U, Sn, Nb	Stable
Quartz	—	—	—	Fe, Mg, Al, Ti, Na, B, Ga, Ge, Mn, Zn	

Note: The above groupings are generalizations; for example, only the allanite variety of epidote contains abundant rare earth (RE) elements, and only some varieties of muscovite will have Rb and Li in the quantities indicated.

From Levinson (1974).

and other factors affecting crystal chemistry. The qualitative rules controlling the substitution of one element for another are discussed by Krauskopf (1979, chapter 5).

The background trace element content of rocks is largely due to trace elements occurring within the common rock forming minerals (e.g. Table 2.5). Modal variations in the rocks may cause considerable variations in the background concentrations, which are unrelated to mineralization, as a result of different trace element concentrations in various rock forming minerals. The trace element content of specific mineral fractions can be used to indicate the geochemical characteristics of rocks. Beus and Grigorian (1977), from studies of the trace element distribution in the different mineral fractions of rocks, defined "mineral concentrators" and "mineral Accumulators". Mineral concentrators contain the maximum amount of a particular element in a rock, while mineral accumulators contain the bulk of the element in the rock. The distribution balance of trace elements in rock forming minerals can be useful during the interpretation of geochemical surveys. High concentrations of Ni in the olivines and pyroxenes of ultrabasic rocks, for example, would indicate the absence of magmatic nickel sulphide mineralization in spite of apparently anomalous concentrations of nickel.

c) Elements present in a soluble (mobile) form.

Trace elements can also occur in gas-liquid inclusions and within capillary and pore solutions in rocks. The elements in gas-liquid inclusions in the vicinity of deposits formed by hydrothermal or aqueous solutions may be used to indicate the composition of the mineralizing solutions, temperature gradients, etc., which may influence the interpretation of primary goechemical patterns.

2.1.5. Associations of elements in mineral deposits.

The economically important elements can be grouped into associations on the basis of their empirically observed tendency to occur together in particular ore types (e.g. Table 2.6). The groupings reflect specific ore forming processes and tectonic settings, rather than the global generalizations of Goldschmidt's classification. Tables of associated elements for particular regions (e.g. for Australia in Joyce, 1976, p 23) are useful for the selection of possible target and pathfinder elements that can be used during geochemical surveys. The actual elements analysed during routine sampling should, however, be based on orientation studies of mineralization in the area of interest.

Table 2.6. Associated elements in some mineral deposits. From Rose, Hawkes and Webb ((1979).

Type of deposit	Major components	Associated elements
Magmatic deposits		
Chromite ores (Bushveld)	Cr	Ni, Fe, Mg
Layered magnetite (Bushveld)	Fe	V, Ti, P
Immiscible Cu–Ni-sulfide (Sudbury)	Cu, Ni, S	Pt, Co, As, Au
Pt–Ni–Cu in layered intrusion (Bushveld)	Pt, Ni, Cu	Cr, Co, S
Immiscible Fe–Ti-oxide (Allard Lake)	Fe, Ti	P
Nb–Ta carbonatite (Oka)	Nb, Ta	Na, Zr, P
Rare-metal pegmatite	Be, Li, Cs, Rb	B, U, Th, rare earths
Hydrothermal deposits		
Porphyry copper (Bingham)	Cu, S	Mo, Au, Ag, Re, As, Pb, Zn, K
Porphyry molybdenum (Climax)	Mo, S	W, Sn, F, Cu
Skarn-magnetite (Iron Springs)	Fe	Cu, Co, S
Skarn–Cu (Yerington)	Cu, Fe, S	Au, Ag
Skarn–Pb–Zn (Hanover)	Pb, Zn, S	Cu, Co
Skarn–W–Mo–Sn (Bishop)	W, Mo, Sn	F, S, Cu, Be, Bi
Base-metal veins	Pb, Zn, Cu, S	Ag, Au, As, Sb, Mn
Sn–W greisens	Sn, W	Cu, Mo, Bi, Li, Rb, Si, Cs, Re, F, B
Sn-sulfide vein	Sn, S	Cu, Pb, Zn, Ag, Sb
Co–Ni–Ag vein (Cobalt)	Co, Ni, Ag, S	As, Sb, Bi, U
"Epithermal" precious metal	Au, Ag	Sb, As, Hg, Te, Se, S, U
Mercury	Hg, S	Sb, As
Uranium vein	U	Mo, Pb, F
Copper in basalt (L. Superior type)	Cu	Ag, As, S
Volcanogenic massive-sulfide Cu	Cu, S	Zn, Au
Volcanogenic massive-sulfide Zn–Cu–Pb	Zn, Pb, Cu, S	Ag, Ba, Au, As
Au–As-rich Fe formation	Au, As, S	Sb
Mississippi Valley Pb–Zn	Zn, Pb, S	Ba, F, Cd, Cu, Ni, Co, Hg
Mississippi Valley fluorite	F	Ba, Pb, Zn
Sandstone-type U	U	Se, Mo, V, Cu, Pb
Red-bed Cu	Cu, S	Ag, Pb
Calcrete U	U	V
Sedimentary types		
Copper shale (Kupferschiefer)	Cu, S	Ag, Zn, Pb, Co, Ni, Cd, Hg
Copper sandstone	Cu, S	Ag, Co, Ni

2.1.6. The mobility of elements in the primary environment.

a) The geochemical migration of elements.

Geochemical migration, as defined by Fersman, is the movement of atoms of the chemical elements within the Earths crust, usually resulting in their dispersion or concentration. Migration of the elements in the primary environment takes place mainly in liquid phases such as magmas and hydrothermal or supercritical aqueous solutions.

b) The mobility of elements in magmas.

The behaviour of elements in magmas is controlled by their partitioning between mobile and immobile phases during magma generation and during crystallization, fractionation and differentiation of magmas. Bowen's reaction series (Fig. 2.2) can be used as an approximation of major and minor elements between a mobile silicate melt and an immobile solid phase in magmas. The early crystallizing elements (e.g. Fe, Mg, Cu and Ti) tend to be less mobile than elements such as Si, Al, Na and K which are enriched in mobile residual fractions. The extent to which elements, including trace elements, are partitioned between mobile and immobile phases is dependent on the temperature, pressure and composition of the melt, as well as the activities of oxygen, sulphur and other volatile components (e.g. H_2O and CO_2). The gravitational properties of elements and minerals are an important factor during crystallization and fractionation of magmas (e.g. the accumulation of platinum and chromite in basic magmas). The laws of crystal chemistry, which are based on a combination of factors including ionic size, valency, chemical bond types and crystal field theory, play a major role in determining the mobility of trace elements in magmatic environments. The basic principles involved are discussed by Anderson (1978) and will not be repeated here. The important conclusion is that certain trace elements (e.g. Ni, Co) will tend to be associated with early crystallizing minerals (e.g. olivine and pyroxene), while elements such as Li, Be, Nb, Tu, Sn, U, Th, W etc. are concentrated in the mobile residual fractions of magmas. The elements commonly occurring in pegmatites are examples of primary mobility in the magmatic environment.

c) The mobility of elements in hydrothermal and aqueous solutions.

The partitioning of elements from the residual fractions of magmas to mobile hydrothermal or supercritical aqueous solutions is the most likely source of the trace elements concentracted in paramagmatic deposits. The solutions migrate away from the magmatic source and transport components such as trace elements, sulphur, chlorine, etc. until changes in the solutions and the geological environment cause the precipitation of

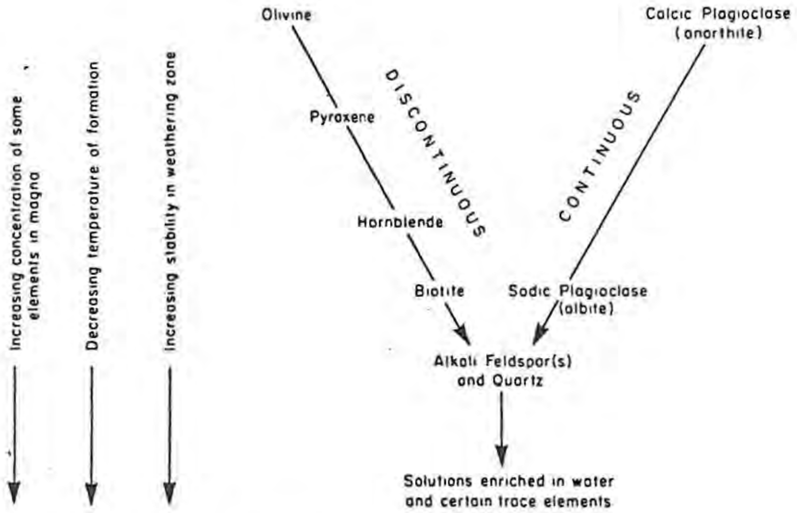


Fig. 2-2. Bowen's reaction series.

From Levinson (1974).

Table 2.7 Selected geochemical barriers. From Beus and Grigorian (1977).

Barrier type	Characteristics
Temperature	This is very important for migration in endogenic processes. The role of this barrier in exogenic processes is insignificant.
Decompression	In endogenic processes an abrupt decrease in the pressure within the system plays a major role in the processes of mineral formation. It is much less significant in exogenic processes.
Acid-alkaline	The effect of changes in the acidity-alkalinity regime of a solution during endogenic processes is sometimes a decisive factor in the separation of many components in the solid phase, and in the concentration of ore substances. It is of less significance in exogenic processes; however, the alkaline barrier is responsible for the precipitation of iron, nickel, and other metals from solution when the solution comes into contact with limestones at the boundary of weakly acidic soil horizons and deeper levels rich in carbonate materials, etc.
Oxidizing-reducing	In endogenic, as well as in exogenic processes, a sudden change in the oxidizing-reducing environments in the paths of migration has a decisive effect on the precipitation of some metals:
a) Oxidizing	takes place as juvenile or ground waters, low in oxygen, come into contact with surface waters rich in oxygen. It is very important in the precipitation of the oxides of iron and manganese in surface waters;
b) reducing hydrogen sulfide	causes precipitation of the majority of metals in the form of sulfides;
c) reducing gley	causes precipitation of some anion-producing metals, such as uranium, vanadium, and molybdenum.
Sulfate and carbonate	Occurs at the initial interaction of sulfate and carbonate waters with other types of waters rich in calcium, strontium, and barium. Gypsum and celestine are formed.
Adsorption	Typically an exogenic geochemical barrier. It is of great importance in the precipitation of trace elements from surface and ground waters.
Evaporation	Occurs in regions of rapid evaporation of ground waters. It is accompanied by salinization, the formation of gypsum, etc.
Mechanical	Results from changes in the velocity of water flow (or air movement) and is responsible for the precipitation of heavy minerals. It plays a major role in the formation of placer deposits.

various minerals. Mineral and element zoning is a common feature of paramagmatic deposits and is dependent on differences in element mobility in hydrothermal solutions. Beus and Grigorian (1977) recognize two classes of factors affecting the primary migration of elements viz. internal and external factors.

The "internal factors" affecting element migration include thermal, gravitational, chemical (particularly the tendency to form complexes) and radioactive properties of atoms. Beus and Grigorian summarize the effects of the chemical properties of elements on their primary mobility, particularly in hydrothermal and supercritical fluids, as follows:

"The migration of elements in natural solutions may, in conformity with the chemical properties of the elements, occur (1) in the ionic form (mainly the strong bases) and also (2) in the form of complex ions binding the amphoteric elements and the complex-forming agents with acidic elements possessing the maximum electronegativity. In this connection two major properties of compounds capable of migration in natural solutions can be specified. These compounds must be soluble and migration-stable to a certain extent i.e. they must not have any tendency to enter into chemical reactions in the specific physicochemical environment."

The external factors affecting the migration of elements in the primary environment include temperature, pressure and the chemical environment of migration. The factors characterize the thermodynomic environment of the medium in which an element migrates and in which the inherent properties of an element are expressed. The chemical environment in which an element migrates is dependent on (1) the internal changes that take place in natural solutions with changes in temperature and pressure and (2) the changes in the composition of the solution caused by reaction with the surrounding rocks.

Deep-seated (endogenic) and surficial (exogenic) geochemical barriers, which result in abrupt changes in the physicochemical environment of element migration, cause the precipitation of certain elements from solution. Geochemical barriers (e.g. Table 2.7) have an important affect on the mobility of elements and their recognition is essential for the interpretation of primary and surficial geochemical patterns.

2.2.0. Primary Geochemical Patterns of Regional Extent.

2.2.1. The geochemical specialization of lithological units.

The geochemical specialization of lithological units implies that the distribution of one or several trace elements in rocks shows specific features, such as higher or lower contentrations of elements or anomalous values of variance of the element content, which are unusual for the given rock type (Beus and Grigorian, 1977). Igneous, matamorphic and sedimentary sequences with which economic concentrations of chemical elements are genetically or paragenetically associated generally exhibit specific chemical features which may differentiate them from barren lithological units of similar composition and appearance. The recognition of these geochemical features can be used during reconnaissance exploration to define potentially metalliferous formations or areas. The geochemical specilization of a lithological unit, however, only indicates the potential for mineralization as the accumulation of economic concentrations of elements depends on the coincidence of favourable geochemical and geological features.

The assesment of the geochemical specialization of lithological units is based on:

a) the trace element distribution patterns in rocks.
b) the trace element distribution in rock forming minerals
c) ratios of the contents of geochemically related elements in rocks and minerals.

The geochemical specialization of rocks is related to all the processes involved in their formation. The trace element characteristics of igneous rocks will thus be dependent on such factors as tectonic setting and magma genesis. The characteristics of sedimentary rocks will depend on the tectonic and climatic factors affecting sedimentation and on the diagenetic alteration of sediments. Metamorphism, metasomatism and hydrothermal activity tend to alter the primary characteristics of rocks and can either mask or enhance trace element patterns related to mineralization.

The extent to which the geochemical characteristics related to ore forming processes can be destinguished from geochemical characteristics related to normal rock forming processes determines the applicability of geochemical specialization in mineral exploration. The following sections are intended to illustrate the factors involved in the use of the geochemical specialization of rocks in mineral exploration and to emphasize the importance of understanding the genesis of mineral deposits and country rocks in order to interpret primary geochemical patterns.

2.2.2. Geochemical and metallogenic provinces.

Beus and Grigorian (1977) define geochemical provinces as "large-scale crustal units characterized by common features of geological and geochemical evolution expressed in the chemical composition of geological formations, as well as in the endogenic and exogenic metalliferous and nonmetalliferous concentrations of the chemical elements." The definition includes the more specific metallogenic provinces, which are regions characterized by concentrations of particular metals or types of ore deposits.

A considerable number of geochemical provinces have been defined on the basis of various regional geochemical characteristics (e.g. Beus and Grigorian, 1977 ; Rose, Hawkes and Webb, 1979, pp 78 - 84), but irrefutable evidence of the existence of the provinces is often lacking due to the large volume of geochemical data required to delineate them. Geochemical and metallogenic provinces may indicate regions with the potential for economic mineralization, but their use to indicate favourable exploration areas is less definitive than the consideration of regional geology and tectonic setting. The presence of significant concentrations of target elements in a region is, however, an important factor in the selection of regional exploration areas.

2.2.3. Geochemical specialization indicating magmatic deposits.

The type of geochemical specialization of volcanic and intrusive rocks which can indicate the potential for associated magmatic deposits is best illustrated by the work done on the regional characteristics of ultrabasic and basic rocks with associated magmatic nickel and copper sulphide deposits. The genesis of magmatic sulphide deposits involves the partitioning of Ni and Cu from ultrabasic and basic magmas by an immissible sulphide fraction (Maclean and Shimazaki, 1976). The regional potential for magmatic sulphide deposits can be recognized by the following features of the source rocks:

a) High Ni and S contents and a Ni to S ratio between 1 : 2 and 2 : 1 was found to be indicative of mineralized ultrabasic and basic rocks by Hausen et al. (1972).

b) Cameron et al. (1971) found that Cu, Ni and to a lesser extent Co are enriched in the sulphide minerals (e.g. pyrite) of potentially mineralized ultrabasic and basic rocks compared to barren rocks in the Canadian Shield (Table 2.8.).

c) The presence of iron sulphides, chrome spinels with high Fe_2O_3 : FeO ratios and local nickel-depleted zones were found to be good indicators of mineralization associated with peridotites in Canada by Naldrett and Gasperini (1971).

Table 2.8

Geometric mean content of sulphur and sulphide-held Cu, Ni, and Co in ore-bearing mineralized, and barren ultramafic intrusions in the Canadian Shield (from Cameron et al., 1971)

	Number of bodies	Number of Samples	Cu, ppm	Ni, ppm	Co, ppm	S, %
ORE groups: (deposits with >5000 tons Ni-Cu)	16	372	67.8	715	57.4	0.166
MINORE group: (deposits with <5000 tons Ni-Cu)	5	91	6.8	560	25.2	0.036
BARREN group:	40	616	6.9	354	31.3	0.031
All deposits:	61	1079	15.2	469	37.9	0.056

2.2.4. Geochemical specialization indicating paramagmatic deposits associated with granitic intrusions.

Discrimination between productive and barren granitic intrusions on the basis of trace element enrichment of the source rock has been attempted in many areas. Tin appears to be the only element that generally (but not universally) shows enrichment in intrusions with associated tin mineralization (Govett and Nichol, 1979). Many workers have observed no clear correlation between the content of other elements (e.g. Cu, Pb, Zn, Mo, W) in granites and associated vein deposits. The lack of correlation is ascribed to the formation of the deposits by processes not directly related to the genesis of the intrusives (Govett and Nichol, 1979).

The form of the frequency distribution of an element in a region or in a particular intrusion is often more diagnostic of mineralization than the mean value of the element content. Garrett (1971) showed that the frequency distribution of W differed between barren and mineralized acidic plutons in the Yukon and Northwest Territories of Canada (Fig. 2.3).

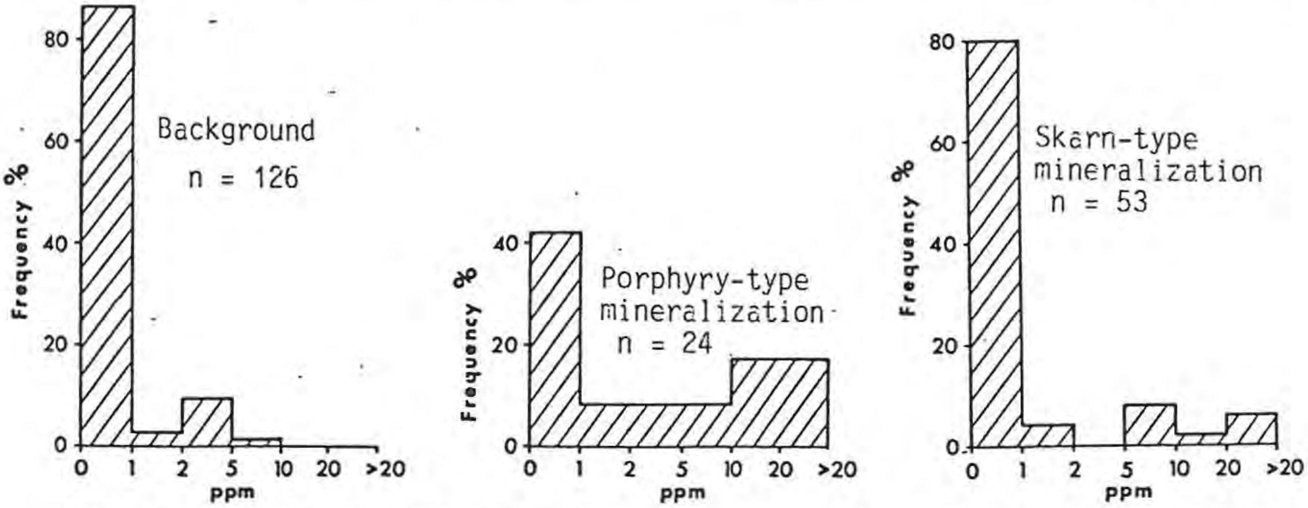


Fig. 2.3. Frequency distribution of W in mineralized and barren granitic intrusions. From Garrett (1971).

The use of variations in the element content of a particular mineral phase to discriminate between barren and productive plutons has also met with mixed results. The major and trace element contents of feldspars, biotite and muscovite from granite bodies with associated tin, copper, zinc and lead mineralization in southwest England showed differencesfrom those in unmineralized granites elsewhere in England and Scotland (Bradshaw, 1967 . The element contents were, however, largely overlapping as a result of differences in the fractionation of the granites. The recognition of intrusions with associated porphyry Cu and Mo deposits and unmineralized stocks, using the trace element content of biotites (Jacobs and Parry, 1976) and multi-element whole rock analysis (Allen et al. 1976), is only successful in cases where actual alteration zones related to the porphyry systems are sampled.

The recognition of barren and productive plutons, during exploration for hydrothermal vein deposits, skarn deposits and porphyry deposits, on the basis of geochemical specialization appears to have limited potential. The partial success attained in many studies indicates that geochemical characteristics related to ore forming processes are seldom the dominant feature of the plutons and they are largely masked by characteristics related to the normal magmatic processes. The use of geological and tectonic criteria and geochemical methods aimed at locating primary dispersion patterns directly related to mineral deposits appears to be a more favourable approach to the recognition of potentially mineralized granitic intrusions.

2.2.5. Geochemical specialization indicating volcanogenic and volcano-sedimentary massive sulphide deposits.

Volcanogenic and volcano-sedimentary massive sulphide deposits are formed by subaqueous exhalitive activity during periods of quiessence in volcanic activity and sedimentation. Deposits tend to cluster at specific levels in the volcanic or sedimentary sequences which are marked by chemical sediments or black shales deposited during the quiessent periods. Broad syngenetic geochemical patterns are preserved by the incorporation of base metals, Mn, Ca and Ba dispersed from the areas of exhalative activity in the chemical sediments and shales. The tendency for volcanogenic and volcano-sedimentary deposits to show spatial as well as stratigraphic clustering makes the recognition of the geochemically specialized exhalite horizons an important reconnaissance method during exploration for massive sulphide deposits (e.g. the Archean volcanogenic deposits in Canada and the McArthur River deposits in Australia).

Volcanogenic massive sulphide deposits, such as the Archean deposits of the Canadian Shield and the Kuroko deposits of Japan, are associated with felsic units of calc-alkaline volcanic sequences. The felsic volcanics of productive calc-alkaline sequences in the Canadian Shield are characterized by slightly higher contents of Fe, Mg and Zn and by lower Na_2O and CaO contents than nonproductive sequences (Govett and Nichol, 1979). Cameron (1974) found that the sulphur content of felsic rocks was higher in productive sequences and lower in nonproductive sequences than the sulphur content of the basic rocks in the same volcanic sequence.

2.2.6. Geochemical specialization indicating sedimentary deposits.

Sedimentary mineral deposits are commonly associated with specific sedimentary facies representing favourable tectonic and depositional environments for the accumulation of the ore elements. The favourable sedimentary units can generally be recognized by geological and sedimentalogical characteristics, but the regional potential of a sedimentary horizon for a specific type of mineralization can also be indicated by higher concentrations of target and pathfinder elements (e.g. the Kupferschiefer in Europe). The geochemically specialized sedimentary horizons are generally anomalous over long strike lengths, but are relatively thin and have sharp contacts with underlying and overlying barren sedimentary units. The use of geochemical specialization can thus be of importance in tracing potential ore horizons in metamorphosed and deformed sedimentary sequences.

Sedimentary sequences with associated Fe and Mn deposits commonly have a facies zoning (i.e. oxide, silicate, carbonate and sulphide facies) which can be used during reconnaissance exploration. A knowledge of the geochemistry of Fe and Mn can be used to predict the distribution of facies which have potential for higher grade ore (e.g. oxide iron facies) and ore which has particular chemical characteristics (e.g. carbonate facies Mn deposits). Geochemical characteristics of sedimentary units formed by the passage of mineralizing solutions during diagenesis (e.g. the alteration tongues related to roll-front uranium deposits) may have important applications during exploratory drilling.

2.3.0. Primary Geochemical Patterns Related to Individual Mineral Deposits.

2.3.1. Factors affecting the characteristics of primary geochemical halos.

The characteristics (e.g. size, shape, intensity and contrast) of primary geochemical patterns associated with individual mineral deposits are dependent on the following factors:

a) The ore-forming processes.

Mineral deposits can be classified on a genetic basis into groups of deposits having broadly similar geological, geochemical and mineralogical characteristics (Table 2.9. and Anderson, 1978, pp 1-5). The characteristics of primary geochemical halos associated with a particular genetic class of mineral deposits (e.g. porphyry or volcanogenic deposits) are largely controlled by the ore-forming process, and deposits of the same genetic type will thus have similar geochemical halos.

Table 2.9.

Classification of mineral deposits From Rose, Hawkes and Webb (1979).

I. *Deposits produced by chemical processes of concentration at elevated temperatures within the earth or at the sea floor*
  A. In magmas (magmatic deposits)
    1. By concentration of crystals from magma (chromite and magnetite of Bushveld complex)
    2. By separation of immiscible sulfide or oxide liquids from magma (Cu–Ni at Sudbury, Ont.; Ti at Allard Lake, Que.)
    3. By crystallization of unusual magmas
      (a) Carbonatites (Nb at Oka, Que.; Cu and phosphate at Palabora, South Africa)
      (b) Pegmatites (Nb–Ta in Nigeria; mica at Petaca, N. Mex.; Li at Kings Mtn, N. Car.)
  B. From hot aqueous fluid formed within the earth (hydrothermal deposits)
    1. Deposited within the earth and associated with intrusive igneous bodies or volcanic centers
      (a) Disseminated sulfides in and adjacent to igneous bodies (porphyry–Cu–Mo deposits of Bingham, Utah)
      (b) Contact metasomatic replacement of carbonate rocks (skarn deposits of Fe at Iron Springs, Utah; Cu–Pb–Zn at Central District, N. Mex.)
      (c) Vein and replacement deposits
        (i) In and adjacent to granitic intrusions (Sn–Cu at Cornwall, England)
        (ii) Peripheral to granitic intrusions (Cu at Magma, Ariz.; Pb–Zn–Ag of Central District, N. Mex.; Pb–Ag of Coeur d'Alene, Idaho)
        (iii) Associated with volcanic centers and hot spring systems on land (Ag at Pachuca, Mexico; Au at Carlin, Nev.)
        (iv) Cu associated with basaltic volcanism (northern Michigan Cu, Mich.)
    2. Deposited within the earth but with no obvious relation to igneous activity
      (a) Pb–Zn sulfide deposits in carbonate rocks (Mississippi Valley deposits, U.S.A.)
      (b) U deposits in sandstones (Colorado Plateau, U.S.A.)
      (c) Cu deposits associated with red sediments (Nacimiento, N. Mex. and White Pine, Mich.)
    3. Deposited on the sea floor by fluids from hot springs
      (a) Massive Fe-sulfides with base and precious metals, in association with volcanism (volcanogenic massive sulfides, Kuroko deposits, Japan)
      (b) Base-metal sulfides unrelated to volcanism (Cu at Ducktown, Tenn.)
      (c) Extensive Fe- and Mn-rich deposits with associated Au and other metals (as in premetamorphic carbonate beds at Homestake, S. Dak.)

II. *Deposits formed by chemical processes of concentration at or near the surface of the earth at low temperatures*
  A. By weathering and related processes on land
    1. By leaching of soluble constituents to leave residual concentrations (bauxite, Fe-, Mn-, and Ni-rich laterites)
    2. By supergene enrichment of sulfides (Cu at Miami, Ariz.)
    3. By evaporation of pore waters from soil (U in caliche at Yeelerie, Australia)
  B. By precipitation in lakes and oceans
    1. By evaporation of water (evaporites, gypsum, halite, borates)
    2. By chemical changes in solution
      (a) Precipitation of limestones and dolomites
      (b) Unusual precipitates (Fe formation, Mn nodules, phosphates, base-metal sulfides)
      (c) By biological processes and diagenesis
        (i) Accumulation of plant debris (coal)
        (ii) Formation of liquid and gaseous products from plant and animal debris (oil and gas deposits)
        (iii) Conversion of sulfates to native sulfur (sulfur deposits)

III. *Deposits produced by mechanical processes of concentration*
  A. Concentration by size in flowing water (gravels, sands, clays)
  B. Concentration of dense minerals by flowing water (placer deposits of Au, Pt, Sn, diamond)

b) The composition of the ore-forming magma or aqueous solution.

The elements concentrated in primary geochemical halos reflect the elements present in the ore-forming magma or solution. The target and geochemically associated trace elements (refer to section 2.1.5.) are normally the best indicators of mineralization, but major and minor element halos can also be developed.

c) The local geology and tectonic setting.

The regional geological and tectonic setting of deposits of a specific genetic type generally shows a considerable degree of similarity but the local geology and tectonic setting of deposits can vary significantly from one region to another and between individual deposits in the same region. The local geological, tectonic and genetic variations can give rise to significant differences in the size, shape, intensity and contrast of primary geochemical patterns associated with particular types of mineral deposits.

d) Post-mineralization tectonic history.

The post-mineralization tectonic history of a mineral deposit can alter the characteristics of primary geochemical halos. Regional metamorphism and structural deformation, in particular, are capable of masking or enhancing primary geochemical patterns and developing patterns unrelated to the original mineralizing processes (e.g. leakage anomalies due to metamorphic dispersion of mobile elements).

2.3.2. Types of primary geochemical halos.

Primary dispersion patterns directly related to mineralization can be broadly classified according to the processes by which they are formed (Bradshaw et al., 1972; Rose, Hawkes and Webb, 1979):

a) Syngenetic halos.

The processes which concentrate elements in mineral deposits may cause a local concentration or depletion of certain major, minor or trace elements in igneous or sedimentary rocks at the same time as the mineral deposit. The principles involved are essentially the same as those discussed for syngenetic regional specialization of rocks (section 2.2.0.), but the local syngenetic halos are more pronounced as the ore forming processes are dominant in the immediate vicinity of mineral deposits.

b) Epigenetic halos.

Epigenetic dispersion patterns (i.e. chemical patterns superimposed on pre-existing country rocks) are typically associated with deposits formed by hydrothermal and aqueous solutions. The solutions forming the deposits are generally in disequilibruim with the surrounding country rocks, resulting in the dispersion of elements from the fluids to the rocks. Bradshaw et al, (1972) recognize three main methods of dispersion:

1) The diffusion of ions through a static medium. The process is responsible for dispersion patterns of limited extent which tend to decay logarithmically with distance from the source of diffusion.

11) Dispersion of elements by the flow of mineralizing solutions (infiltration) through micro- and macro-fractures which tends to form irregular but generally more extensive dispersion patterns.

111) Selective replacement of minerals which involves both diffusion and infiltration.

The formation of epigenetic halos by the processes of diffusion, infiltration and alteration is controlled by a large number of factors such as pressure and temperature gradients; composition of the ore forming solutions; composition, reactivity and permeability of the country rocks; the structure and extent of fracturing of rocks (including hydrofracturing) etc. The characteristics of the halos are thus highly variable. Three broad categories of epigenetic patterns can, however, be defined viz. wall rock anomalies, leakage anomalies and alteration halos.

The diffusion, precipitation and adsorption of ions moving outward from the centre of mineralization tends to form three dimensional, non-symmetrical wall rock anomalies around an ore body. The characteristics of the wall rock anomalies depend on the rate and extent of diffusion which is largely controlled by the following factors:

1) The concentration of anomalous elements in the ore-forming solutions and variations in the concentration with time. Movement of the fluids past the centre of mineralization also results in variations in element concentration at the source of diffusion.

11) The length of time that diffusion operates. The diffusion process is slow and long periods of disequilibrium between ore-forming fluids and wall rocks are necessary for the formation of significant aureoles.

111) The temperature and pressure gradients between the ore--forming fluids and the country rocks.

1V) The type and characteristics of the wall rocks. Reactive wall rocks (e.g. dolomites or limestones) tend to have narrow aureoles, while weakly reactive rocks with high porosity and permeability favour wider aureoles.

V) The diffusion constant (Rose, Hawkes and Webb, 1979, pp 78-100) of the elements involved. In general, small ions and high temperatures favour the formation of large aureoles.

Leakage anomalies are formed by the migration of ore forming fluids along channelways in the vicinity of mineral deposits precipitated from hydrothermal or aqueous solutions. The location, dimensions and intensity of leakage anomalies depend on the following factors (discussed by Rose, Hawkes and Webb, 1979 pp 101-104):

1) The path of flow of the ore fluid.

11) The amounts of indicator elements in the ore fluids.

111) The controls on precipitation, adsorption, and other processes transfering indicator elements from the hydrothemal fluids to the rocks.

The leakage anomalies may consist of visible ore related minerals or of dispersed trace elements deposited in fracture zones or permeable rocks above, below or adjacent to paramagmatic or sedimentary deposits formed by hydrothermal or aqueous solutions. Leakage anomalies formed by ore fluids which had precipitated a major part of their ore forming elements and moved past the centre of mineralization, normally occur above the mineral deposit and are favourable indicators of blind deposits. Leakage anomalies may, however, also be formed by fluids which did not encounter the correct conditions for the precipitation of ore, by fluids which had not reached a favourable site for the concentration of mineralization, or by fluids that lacked the potential to form ore.

c) Alteration halos.

The infiltration of hydrothermal and aqueous solutions and diffusion of ions from the solutions can alter the mineralogical constitution of rocks. The processes may result in the alteration of existing minerals or the formation of secondary minerals. Alteration can take place with or without detectable changes in the major or trace element content of the rocks. The changes in the mineralogy and texture of wall rocks enclosing ore are often more extensive than the ore itself and can act as a guide to orebodies as well as an indicator of the original ore-forming solutions. The effects of alteration are generally visible in outcrop and under the microscope, but chemical methods may also be used to study the characteristics of alteration patterns.

The alteration halos around paramagmatic deposits (e.g. porphyry deposits and hydrothermal vein deposits) tend to be well developed and often have mineralogical zoning patterns related to temperature gradients and distance from the source of mineralization. The subject of hydrothermal alteration is discussed by Rose and Burt (in Barnes, 1979, pp 173-277).

d) The zoning of mineral deposits and primary geochemical halos.

The chemical and mineralogical zoning of orebodies and the primary geochemical halos associated with them is a common feature of mineral deposits. The zoning is caused by:

1) differences in the mobility of elements.

11) changes in the composition of magmas, hydrothermal solutions or aqueous solutions responsible for the formation of mineral deposits.

111) spatial and temporal changes in the physicochemical environment in which ore forming processes are operative. The changes in the physicochemical environment can affect the mobility of elements and the composition of ore-forming magmas or fluid phases.

The geochemical patterns associated with individual mineral deposits are generally formed by a combination of processes and various types of halos tend to overlap. The geochemical signature of specific types of mineral deposit thus comprises a combination of primary geochemical halos which all contribute to the geochemical patterns that can be used to predict, locate and evaluate individual mineral deposits. The major characteristics of the geochemical patterns associated with some types of magmatic, paramagmatic and sedimentary deposits are illustrated in the following sections. The interpretation of geochemical surveys should, however, be based on a thorough evaluation of the geochemical characteristics of the type of mineral deposit sought, with particular reference to the effects of local geological and tectonic factors on the characteristics of geochemical halos.

2.3.3. Primary geochemical halos associated with magmatic deposits.

Magmatic deposits generally do not have clearly defined primary geochemical halos, although syngenetic indications of the proximity of ore may be developed in some situations as illustrated by the following examples:

a) Layered basic and ultrabasic intrusions.

Accumulations of chromite, platinum and Ni-Cu sulphides in layered intrusions (e.g. the Bushveld Igneous Comples) can be indicated by compositional and mineralogical layering of the intrusion and by slight increases in the concentration of target elements in the zones containing mineralized layers. Significant concentrations of the target elements e.g. Cr, Pt, Ni and Cu are, however, largely confined to the mineralized layers and to narrow halos in the immediate vicinity of mineralized layers (e.g. the Merensky Reef).

b) Magmatic Ni-Cu sulphides.

Primary geochemical halos associated with magmatic Ni-Cu sulphide deposits are highly unpredictable. The characteristics of geochemical patterns in the vicinity of massive sulphide mineralization depend on the processes which operated in the magma to concentrate immiscible sulphide droplets which tend to form throughout the magma. Some sulphide deposits may, thus, have no noticeable halos, while the processes of filter pressing and gravity percolation of immiscible sulphide could form significant aureoles of target elements and minerals in other situations.

2.3.4. Primary geochemical halos associated with paramagmatic deposits

Paramagmatic deposits typically have well developed syngenetic and epigenetic halos formed by the dispersion of elements form the mineralizing hydrothermal fluids. The features of the halos are primarily controlled by ore forming processes and various genetic classes of paramagmatic deposits are characterized by distinctive syngenetic and epigenetic primary geochemical patterns. The characteristics of the primary halos are illustrated by reference to some of the more important types of paramagmatic deposits.

a) Porphyry deposits.

Porphyry-type ore deposits are formed by the outward migration of hydrothermal solutions from crystallizing high level calc-alkaline prophyry stocks (Burnham, in Barnes, ed., 1979). The porphyry-type hydrothermal systems are characterized by alteration and mineralization zoning (Lowell and Guilbert, 1970) which can be detected by visible alteration patterns and by the distribution of major and trace elements in the porphyry stocks and country rocks.

Geochemical dispersion patterns associated with Cu-Mo porphyry deposits studied by Olade and Fletcher (1976) and Chaffee (1976) show the following features:

1) Geochemical dispersion in the proximity of the Cu-Mo deposits is related to primary lithology, hydrothermal alteration and mineralization.

11) Trace elements show more useful anomalies than the major elements. Elements associated with mineralization (e.g. Cu, S, Mo, B) can indicate whether a prophyry system is barren or mineralized. Anomalous halos of Cu, S and B extend beyond the alteration zones and constitute larger targets than the visible alteration halos (Table 2.10).

111) The distribution of elements closely related to alteration (e.g. Rb, Sr, Ba) offers an objective and unbiased method of mapping alteration-mineralization zoning and of determining the level of exposure of porphyry systems.

1V) Element ratios are more consistent indicators of mineralization than single element patterns which show erratic trends caused by mineralogical variations.

V) Leakage halos of a wide range of elements (e.g. Ag, Pb, Zn, Mg and Mn) may be developed along major structures (i.e. faults, breccia pipes, etc.) and are a useful guide to ore.

Lithogeochemical data on the distribution of major and trace elements around porphyry-type deposits is reviewed and summarized by Govett and Nichols (1979).

Table 2.10. Comparison of Anomaly Extent and Contrast for Selected Elements. From Olade and Fletcher (1976).

Element	Bethlehem JA		Valley Copper		Lornex		Highmont	
	E[1]	C[2]	E	C	E	C	E	C
Cu	***	5	***	5	***	5	***	5
S	***	5	***	5	nd	nd	nd	nd
Mo	*	2–5	*	2–5	*	5	*	5
B	*	1–2	0		***	2–5	***	2–5
Hg	**	5	0		nd	nd	nd	nd
Rb	**	1–2	**	1–2	nd	nd	nd	nd
Sr[3]	**	1–2	**	1–2	**	1–2	**	1–2

nd: Not determined.

[1] Extent: 0: No anomaly.
*: Anomaly confined to ore zone.
**: Anomaly within alteration envelope.
***: Anomaly beyond alteration envelope.

[2] Contrast: Approximate anomaly to background ratio.

[3] Negative anomaly.

b) Polymetallic vein and replacement deposits.

The distribution of elements (particularly chalcophile elements) around vein, replacement and skarn deposits has been intensively studied by Russian geologists (e.g. Beus and Grigorian, 1977). The work has indicated that these paramagmatic deposits typically have extensive trace element halos with characteristic zoning patterns. The halos extend for large distances (up to hundreds of meters from the ore deposits) in the direction of flow of the hydrothermal solutions (axial zoning). Narrower, but similar, zoning patterns are developed at right angles to the direction of flow (transverse zoning). The halos formed by different elements and halos around different deposits tend to vary in extent, but they form much larger exploration targets than the orebodies (Fig. 2.4.). The target elements normally form the widest halos.

The sequence of elements in the zoned halos is dependent on the mobility of the elements involved and is generally similar for various deposits. Beus and Grigorian (1977) give a large number of examples of zoned trace element halos and discuss methods of interpreting the zoning patterns which can be effectively used to:

1) locate blind deposits.

11) predict whether halos indicate economic concentrations of elements.

111) indicate whether the zoning pattern was developed above or below economic mineralization.

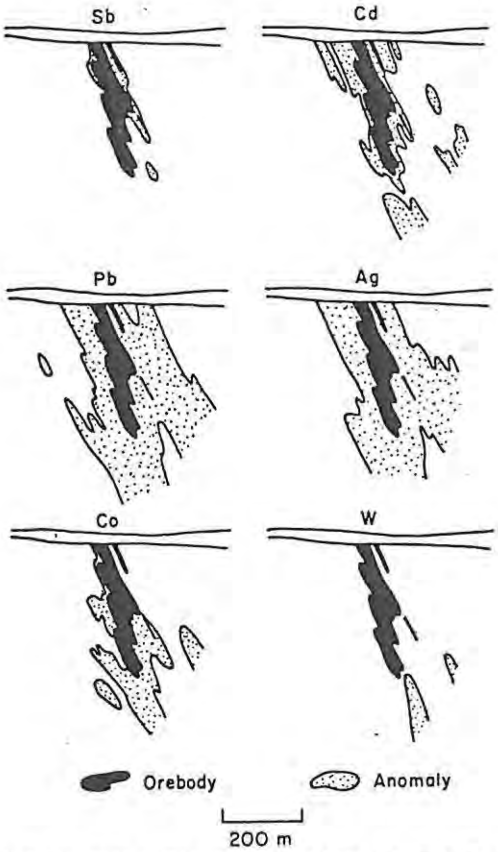


Fig.2.4. Anomalies for trace metals at Harpenberg Pb–Zn–Cu–Ag skarn deposit in Sweden. (After Beus and Grigorian, 1977.)

c) <u>Volcanogenic massive sulphide deposits</u>.

Geochemical patterns in the vicinity of volcanogenic massive sulphide deposits are characterized by three types of primary halos (Fig. 2.5):

1) Local major and trace element concentrations in pre-ore volcanic sequences (similar to the geochemical specialization discussed in section 2.2.5.) can indicate the proximity of mineralization, but are generally of less importance than geological indicators (e.g. rhyolite domes, volcanic breccias, etc.).

11) A stockwork and replacement zone of veins and alteration occurs below the stratiform massive sulphide lenses of proximal deposits. The stockwork zone and the country rocks in the immediate vicinity of the deposits are generally enriched in Mg, Al, Fe and K and depleted in Na and Ca (Govett and Nichol, 1979). Trace element halos (e.g. Cu, Pb, Zn and other elements associated with the mineralization) occur in the altered stockwork zone and may extend into pre-ore volcanics, although the wall rock anomalies are generally of limited extent (a few tens of meters). Alteration and element dispersion patterns may occur in the post-ore rocks above the stratiform orebodies in situations where hydrothermal activity continued during renewed volcanism or sedimentation.

111) Significant halos of ore related elements (e.g. Zn, Cu, Pb, Ba, Hg, Mn, Bi, etc.) occur in the ore equivalent stratigraphic horizons which tend to grade into the ore bodies. The syngenetic geochemical halos were caused by the mixing of ore forming solutions and sea water and the dispersion patterns are generally good indicators of mineralization.

Govett and Nichol (1979) give a summary of lithogeochemical studies done on primary dispersion halos associated with volcanogenic massive sulphide deposits.

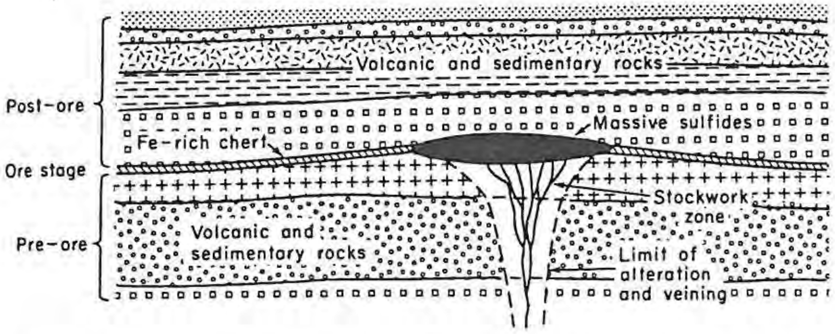


Fig. 2.5. Generalized relationship of massive-sulfide ore to Fe formation, stockwork zone, and post-ore volcanic and sedimentary rocks. From Rose, Hawkes and Webb (1979)

2.3.5. Primary geochemical halos associated with sedimentary deposits.

Mineral deposits in sedimentary rocks may be formed by syngenetic or epigenetic chemical precipitation from aqueous solutions or by the physical accumulation of ore minerals derived by the erosion of source rocks. The characteristics of the geochemical halos associated with the deposits depend on the ore forming process and on the characteristics of the depositional environments as illustrated by the following examples:

a) Volcano-sedimentary and sedimentary base metal deposits.

Volcano-sedimentary and sedimentary base metal deposits are tabular stratiform bodies which often have a considerable continuity of mineralization along strike. The precipitation of ore from metalliferous solutions in favourable sedimentary environments during sedimentation tends to form gradational geochemical patterns representing the transition from ore to barren rocks along strike. The geochemical halos are generally zoned due to differential mobility of indicator elements in the sedimentary environment. Epigenetic halos may be developed in overlying and underlying units if the ore forming process involved the infiltration of solutions into the sediments during sedimentation or diagenesis (e.g. hydrothermal alteration zones associated with some volcano-sedimentary deposits), but geochemical halos are normally confined to the ore horizon.

b) Sulphide deposits in carbonate sequences.

Base metal (e.g. Pb, Zn, Cu) sulphide ores in carbonate rocks are precipitated from metalliferous solutions in favourable traps (e.g. karst systems, carbonate reef complexes, fault zones, etc.). The deposits typically show very limited primary halos which seldom extend beyond the permeable zones (e.g. faults, solution collapse breccias, etc.) along which the mineralizing solutions migrated. The limited geochemical dispersion is due to greatly reduced element mobility in the limestones and dolomites caused by their reactive nature and by the Eh and pH conditions formed by carbonate reactions.

c) Detrital and residual sedimentary deposits.

Placer and alluvial deposits are formed by the accumulation of resistant minerals and elements during the processes of weathering, erosion and sedimentation in the surficial environment (discussed in the following chapter). Geochemical halos related to detrital sedimentary deposits can include:

1) increased concentrations of ore and indicator minerals and elements in sedimentary units formed at the same time as the deposits.

11) zones containing pathfinder elements and minerals formed in the vicinity of deposits by differential mobility during physical dispersion.

3.0.0. GEOMORPHOLOGICAL FACTORS

Muir's Law: "When we try to pick out anything by itself
we find it hitched to everything else in
the universe". (Bloch, 1980).

3.1.0. Secondary Geochemical Patterns in the Surficial Environment.

3.1.1. The surficial environment - introduction.

"The surficial environment is the environment of weathering, erosion and sedimentation at the surface of the earth. It is characterized by low pressure, free movement of solutions, and abundant free oxygen, water and carbon dioxide". (Rose, Hawkes and Webb, 1979). The planning, execution and interpretation of geochemical surveys must take into account not only the geological aspects of the mineralization sought, but also the aspects of the surficial environment that place constraints on the type, magnitude and extent of secondary geochemical anomalies.

The surficial environment is a dynamic system in which the active processes and controlling factors are complexly interrelated. The driving force of the system is tectonic activity which exposes igneous, metamorphic and sedimentary rocks to the processes active in the surficial environment. The rocks and their contained mineral deposits and primary geochemical halos are unstable in the surficial environment. The original materials are reconstitued into new forms by the processes of weathering, soil formation, erosion, transport, and deposition. The agents causing these processes are the components of the hydrosphere, biosphere and atmosphere as well as gravity, temperature and atmospheric pressure. The major controlling factors are the original rock composition, relief, climate, vegetation and time.

The use of material from the surficial environment for exploration geochemistry is based on the fact that anomalous concentrations of indicator elements associated with mineral deposits are reflected by secondary dispersion halos. The simplest types of dispersion halos are developed in an environment of in situ weathering of bedrock to form a residual soil profile (Fig. 3.1) and will be used to illustrate the basic factors which must be considered during the interpretation of geochemical surveys. The basic factors are weathering and element mobility, soil formation, ground water movement, and erosion and transport of surficial material. The factors which can complicate or mask the basic

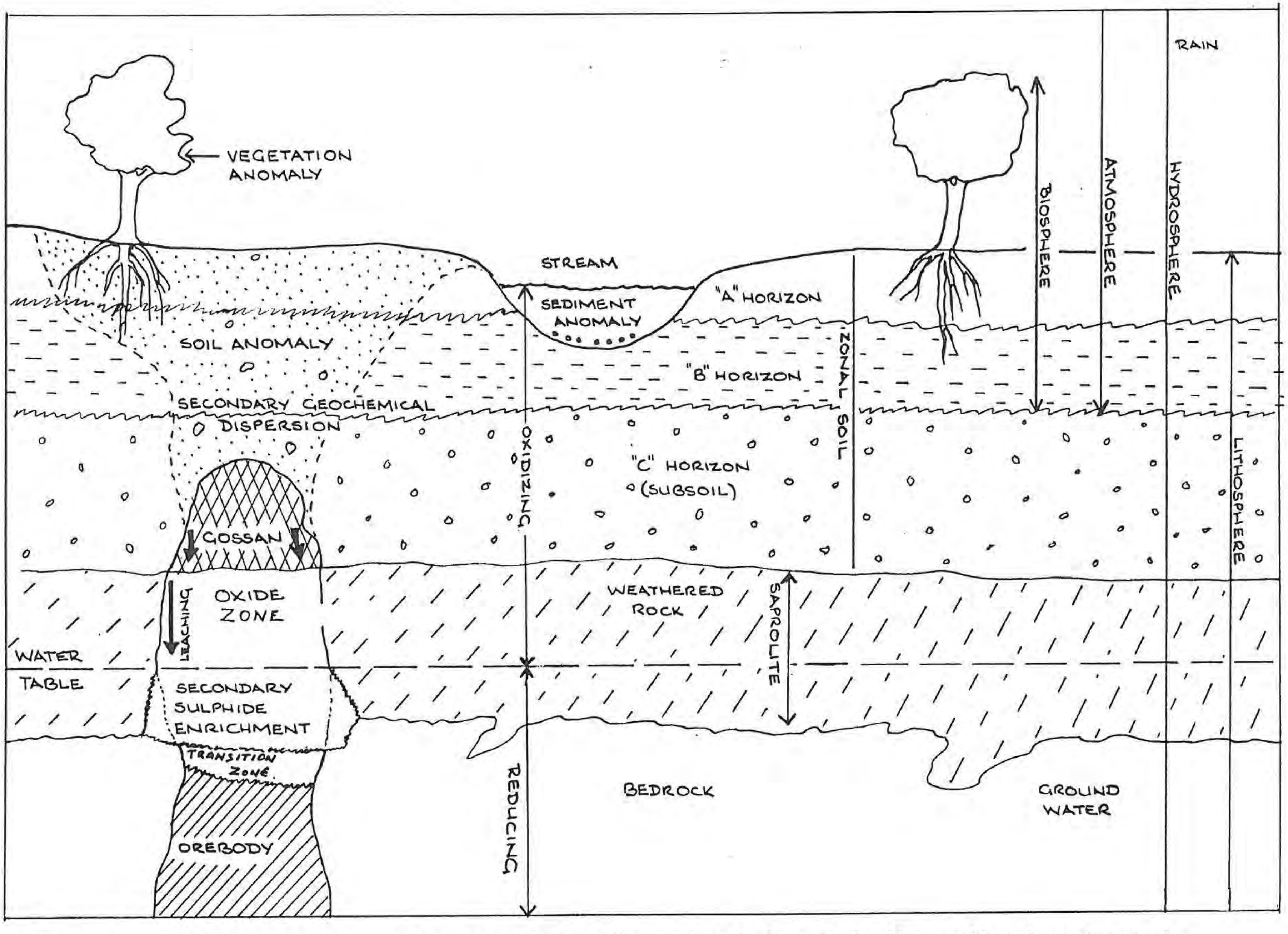


Fig. 3.1. Residual dispersion halos associated with a mineral deposit in the surficial environment.

geochemical patterns, as well as those which cause false geochemical anomalies, are discussed seperately. These factors include the composition of bedrock and mineral deposits, the level of exposure of mineral deposits, relief, climate, vegetation, soil types and compositions, deep weathering profiles, transported overburden and contamination.

3.1.2. The weathering of rocks and mineral deposits.

Weathering is the process of adjustment of rocks and minerals, formed in the primary environment, to the conditions prevailing in the surficial environment. Chemical weathering involves the reaction between rocks and minerals and the constituents of air and water at low temperature and pressure. Physical weathering is the process of fragmentation of rocks with little or no chemical change. Chemical weathering is the dominant form of rock disintegration with physical weathering generally being a subordinate process. Physical weathering is, however, the dominant form of weathering in very cold and/or dry climates and in areas of rugged topography.

Chemical weathering is largely dependant on the presence of moisture. Water is an active agent of weathering and also holds substances in solutions which react with the rock forming minerals. The more important of these substances are oxygen, carbon dioxide, organic acids, and nitrogen acids. Many of the dissolved substances lower the pH of the water making it a better solvent of rock materials. The various agents of chemical weathering function together to cause the decomposition of rocks by the processes of solution, hydration, acid attack and oxidation.

Oxidation plays a dominant role in the weathering of most mineral deposits, which is generally more complex than the weathering of rocks, due to the presence of substantial amounts of iron, manganese, sulphur and trace metals which have more than one oxidation state. The order of resistance to chemical weathering of the ore minerals is generally:

Oxides, silicates, carbonates and sulphides.

The sulphides are particularly susceptible to weathering and sulphide bearing deposits are generally deeply weathered. Krauskopf (1979) summarizes the chemical weathering of sulphide minerals as follows:

a) the metal ions go into solution or into insoluble compounds which are stable under surface conditions.

b) sulphide ions are converted to sulphate ions.

c) relatively acid solutions are produced.

The common oxidation reactions which take place during the weathering of mineral deposits are given by Krauskopf (1979) and Levinson (1974). The processes of chemical weathering cause a fractionation of the ore-forming and associated elements, and may destroy an existing mineral deposit, produce one from previously barren or sub-economic rock or merely change the mineralogy of the deposit depending on the materials, environments and products involved.

The topic of weathering is covered in most text books on applied geochemistry and soils. Summary discriptions of the agents and processes involved are given by Krauskopf (1979), Levinson (1974), Rose, Hawkes and Webb (1979), and Birkeland (1974). The reader is referred to these texts for details of the weathering of rocks and mineral deposits.

3.1.3. The products of weathering and element mobility in the surficial environment.

The products of weathering can be grouped into three categories, viz. residual primary minerals, insoluble minerals formed in the secondary environment (exogenic minerals) and soluble constituents.

a) Residual primary minerals.

Primary minerals are all unstable to some degree in the surficial environment. The quantity and type of residual primary minerals in surficial material is, thus, dependant on the resistance of various minerals to physical and chemical weathering, and on the degree to which weathering has taken place. The structure (eg. cleavage planes) and hardness of minerals controls their physical disintegration. The chemical composition of minerals, as well as their susceptibility to physical disintegration, controls the rate of chemical weathering under a given set of secondary conditions.

The relative susceptibility to weathering of the common silicate minerals in igneous rocks (Table 3.1) is the inverse of their normal sequence of crystallization from magmas. Minerals, such as quartz, zircon, titanium-oxides, and tourmaline, which decompose very slowly in most secondary environments, tend to become more abundant in surficial material during normal weathering. The resistant minerals do, however, decompose under prolonged conditions of extreme chemical weathering.

Table 3.1.

The common rock-forming silicate minerals arranged in their general order of crystallization from magmatic melts, their susceptibility to weathering, and their occurrence in various igneous rock types

Sequence of crystallization	Susceptibility to weathering	Dark minerals	Light minerals	Rock types	
				Volcanic	Intrusive
early	least resistant	Olivine $(Mg,Fe)_2SiO_4$	Calcic plagioclase (anorthite) $CaAl_2Si_2O_8$		
		Augite $Ca(Mg,Fe,Al)(Al,Si)_2O_6$	Calcic plagioclase (labradorite) with sodium	basalt	gabbro
		Hornblende $(Ca,Na,Fe,Mg,Al)_7(Al,Si)_8O_{22}(OH)_2$	Sodium plagioclase with calcium (andesine, oligoclase)	andesite	diorite
			Sodium plagioclase (albite) $NaAlSi_3O_8$	latite	monzonite
		Biotite (dark mica) $K(Mg,Fe)_3(Al,Si_3)O_{10}(OH,F)_2$	Potash feldspar (orthoclase, microcline) $KAl_2Si_3O_8$	rhyolite	granite
			Muscovite (white mica) $KAl_2(Al,Si_3)O_{10}(OH,F)_2$		
late	most resistant		Quartz, SiO_2		

From Hunt (1972).

Ore minerals which are commonly resistant to physical and chemical weathering include oxides (eg. cassiterite, rutile, magnetite, chromite, and ilmenite), native elements (eg. gold, platinum, and diamond), some silicates (eg. beryl) and a few other chemical types such as phosphates (eg. monazite). The hardness (or ductility and malleability), lack of cleavage and generally high specific gravity of the ore minerals which are resistant to physical weathering results in their concentration in placer deposits during soil formation, erosion, and transport. Chemically resistant minerals which cannot withstand physical abrasion, such as wolframite, scheelite, and barite, can accumulate as in situ weathering products, but are broken up during mechanical transport. Chemically unstable minerals, such as sulphides, may be protected from chemical weathering by inclusion in resistant minerals (eg. quartz fragments) and thus occur as meta-stable residual weathering products.

Table 3.2. Relative stability minerals in residual weathering products. From Hunt (1972).

Relative stabilities of minute grains (diam. < 1 mm) of common minerals in surface deposits

Oxides and hydroxides	
Magnetite, Fe_3O_4	Not very persistent in most surface deposits; usually alters to the red hematite, brown geothite, or yellow limonite; stable under anaerobic conditions
Hematite, Fe_2O_3	
Goethite, $Fe_2O_3 \cdot H_2O$	
Limonite, a mixture of oxides, approximately $2Fe_2O_3 \cdot 3H_2O$	Most persistent form; a mixture of the iron oxides and hydroxides
Corundum, Al_2O_3	Rare primary mineral that resists abrasion and is not acted upon by acids; persists in deposits derived from some metamorphic rocks
Diaspore and boehmite, $Al_2O_3 \cdot H_2O$, and gibbsite, $Al_2O_3 \cdot 3H_2O$	Secondary minerals in surface deposits and soils where alumina has been freed by alteration of aluminum-bearing silicates
Titanium compounds	
Anatase and rutile, TiO_2	Persistent
Ilmenite, $FeO \cdot TiO_2$	Moderately persistent
Perovskite, $CaO \cdot TiO_2$, and doelterite (leucoxene), $TiO_2 \cdot H_2O$	Alteration products of sphene (= titanite, $CaTiSiO_5$) and ilmenite (resistant) in surface deposits and soils
Sulphides	
Pyrite, FeS_2	Unstable
Phosphates	
Apatite, $Ca_5(PO_4)_3(F,Cl,OH)$	Moderately persistent; primary
Crandallite, hydrous calcium-aluminum phosphate	Alteration product of apatite; alters to wavellite
Wavellite, $Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$	Secondary
Monazite, rare earth phosphate	Persistent; primary
Carbonates (mostly secondary)	
Calcite (limestone, also aragonite), $CaCO_3$	Soluble; primary or secondary
Dolomite, $CaCO_3 \cdot MgCO_3$	Less soluble than calcite; primary or secondary
Sodium carbonate minerals	Several, mostly with combined water; highly soluble; secondary
Sulfates (mostly secondary)	
Gypsum, $CaSO_4 \cdot 2H_2O$	More soluble than calcite
Anhydrite, $CaSO_4$	Like gypsum
Sodium sulfate and mixed sodium-calcium sulfate	Several, mostly with combined water; readily soluble
Chlorides (secondary)	
Halite, $NaCl$	Highly soluble
Ammonium chloride, NH_4Cl	Highly soluble
Nitrates, nitrites (secondary)	
Soda niter, $NaNO_3$	Highly soluble
Saltpeter, KNO_3	Highly soluble
Silica	
Quartz, SiO_2	Mostly primary; highly resistant to abrasion and solution
Chalcedony, SiO_2	Microcrystalline; also known as chert, flint, jasper; less stable than quartz; primary or secondary
Opal, $SiO_2 \cdot nH_2O$	Least stable form of silica; mostly secondary in surface deposits and soils
Silicates (the principal rock-forming minerals)	
Aluminum silicates without iron or magnesium (light minerals)	
Feldspars	
Potash feldspars: orthoclase, microcline, $KAlSi_3O_8$	Most persistent of the feldspars
Soda-lime feldspars: plagioclase	Gradational series ranging from lime feldspar (anorthite), $CaAl_2Si_2O_8$, to soda feldspars (albite), $NaAlSi_3O_8$; pure end members rare; soda-lime feldspars (oligoclase, andesine) more stable than the lime-soda ones (labradorite, bytownite)
Muscovite (white mica), $KAl_2(Al,Si_3)O_{10}(OH,F)_2$	Primary; stable
Aluminum silicates with or without iron or magnesium	
Clay minerals (the principal secondary minerals in surface deposits and soils; also primary; stable)	
Kaolinite, $Al_2Si_2O_5(OH)_4$	Most stable clay mineral
Illite	Complex hydrous white mica; alters to kaolinite or montmorillonite
Vermiculite	Complex hydrous biotite; alteration product of chlorite and biotite, and alters to kaolinite or montmorillonite
Chlorite	Complex; mostly a primary mineral in surface deposits and soils (i.e., relict from parent rock); least stable of the clay minerals; alters readily to any or all of the others
Montmorillonite	Complex swelling clay that readily absorbs iron, magnesium, calcium, sodium, hydroxyl, or other ions; alters to kaolinite; alteration product of chlorite, vermiculite, and illite
Aluminum silicates with iron, magnesium, or calcium (dark minerals); all primary in surface deposits and soils	
Biotite (dark mica), $K(Mg,Fe)_3(Al,Si_3)O_{10}(OH,F)_2$	Most easily weathered of the dark minerals; readily altered to vermiculite
Hornblende: one of a series of minerals called amphiboles, $(Ca,Na,Fe,Mg,Al)_7(Al,Si)_8O_{22}(OH)_2$	More persistent than augite
Augite: one of a series of minerals called pyroxenes, $Ca(Mg,Fe,Al)(Al,Si)_2O_6$	More persistent than olivine
Olivine, $(MgFe)_2SiO_4$	Least persistent of the dark minerals
Tourmaline, garnet	Persistent
Magnesium silicate	
Serpentine, $Mg_6Si_4O_{10}(OH)_8$	Primary or secondary; stable

b) Secondary minerals.

The secondary (or exogenic) minerals in surficial material are formed by the precipitation of elements freed during weathering and by partial alteration of primary minerals. Secondary minerals include fine grained aluminosilicate clay minerals, and iron, manganese and aluminium oxide clays, as well as insoluble secondary oxides, carbonates, sulphates, chlorides, silicates and native metals. The stability of various secondary minerals is largely dependent on the physical and chemical conditions in the weathering environment. The relative stabilities of minerals (including the secondary minerals) in residual weathering products is summarized in Table 3.2.

The clay minerals, which are the principal secondary minerals in many surficial deposits, are hydrated silicates of aluminium, iron and magnesium arranged in various combinations of tetrahedral and octahedral sheets. Variations in the combination of sheep structures and in their chemical composition (Krauskopf, 1979; Rose, Hawkes and Webb, 1979; and Birkeland, 1974) gives rise to a large number of clay minerals with different chemical and physical properties. Silicon and aluminium form the basic framework of the clay minerals. The presence of Si and Al in solution, which depends on the rate of their release by weathering from primary minerals and more importantly on the rate of leaching from surface environments, controls the amount and type of clay minerals formed. The presence of other cations, largely dependent on the rock types being weathered and the degree to which the cations are mobile in the secondary environment, also controls the type of clay mineral formed. The sequence of formation of clay minerals, in relation to the degree of weathering and to the primary aluminosilicate minerals present, is shown in Fig. 3.2. The formation of Kaolinite is favoured by extensive leaching and removal of Na^+, Ca^{++}, Mg^{++}, K^+, and many trace elements in acidic, well drained environments. Montmorillonite is formed in neutral to alkaline environments, such as occur in waterlogged ground or semi-arid regions, which have incomplete leaching and retention of bases.

The small grain size of clays and their ability to adsorb cations have important affects on the distribution of trace elements in the surficial environment. The clay particles are generally within the size range of colloids, and can thus be suspended in water for long periods and flocculated by electrolytes. They have variable cation exchange capacities which allow them to absorb ions, including some trace metals, from solution. The adsorbed irons are weakly bonded and may be replaced by others when the concentration of the solution changes. The cation exchange capacity of clays increases with pH and montmorillonite, in aklaline conditions, is thus capable of adsorbing significant amounts of trace metals. The presence of clays in surficial materials, especially montmorillonite, decreases their permeability.

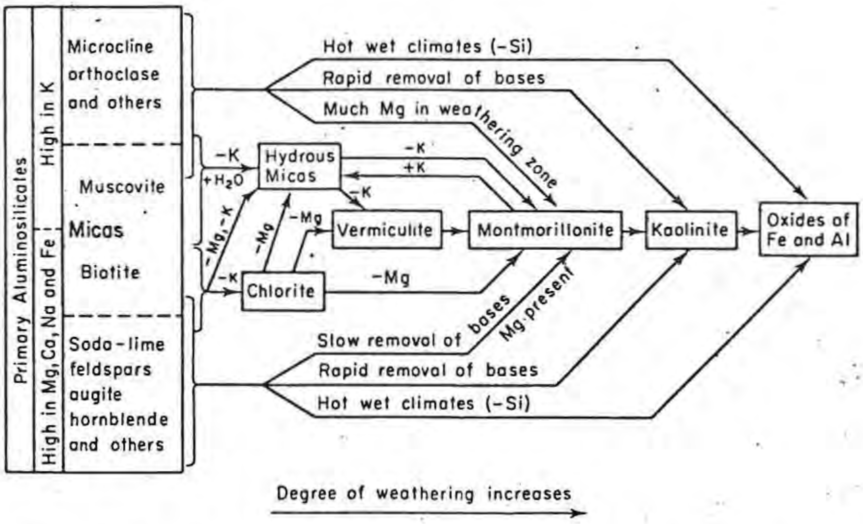


Fig. 3.2. Weathering products of primary minerals, and the sequence of forming clay. From Rose, Hawkes and Webb (1979).

Iron, aluminium and manganese, released during weathering, are insoluble under the normal pH and Eh conditions of the surficial environment and form secondary oxide and hydroxide minerals. (Table 3.2) The ubility of the hydrons oxides, which are common products of weathering, to adsorb or co-precipitate trace metals makes them an important factor affecting the distribution of trace metals in the surficial environment. The geochemical properties of iron, aluminium, manganese and silica, and their relative solubilities under different pH and Eh conditions in the surficial environment, as well as the accumulation of insoluble Fe and Al oxides, silica, and Ca and Mg carbonates to form duricrusts, and the effects of the duricrusts on geochemical exploration, are discussed in detail by Friggins (1979).

Gossan, massive residual hydrous Fe-oxides (limonitic material) with some quartz, secondary silica and clay, is a common weathering product of Fe-bearing sulphides and carbonates. The mineral composition of the gossan depends on the degree of oxidation and leaching. The original sulphide (eg. pyrite, marcasite, pyrrhotite, arsenopyrite, chalcopyrite) and carbonate (eg. siderite and ankerite) minerals may be completely destroyed and the ore metals completely leached. Gossans derived from economic sulphide deposits may, thus, be similar to the ironstones formed by normal weathering concentrations of insoluble Fe-oxides. The weathering of sulphide deposit and the nature and composition of the gossans formed are reviewed by Blain and Andrew (1977).

A wide variety of secondary minerals can be formed in the zone of oxidation during the weathering of mineral deposits (Table 3.3.). The minerals formed depend on the chemical and physical conditions in the weathering environment, and on the original composition of the deposit and the country rock. The secondary minerals are generally crystalline and once formed they tend to be resistant to chemical decomposition. They are not as easily dispersed as clay minerals, but fragments of secondary ore minerals are common in residual surficial material near ore deposits.

c) Soluble products.

The constituents released by the decomposition of primary minerals, which are not required for the formation of insoluble minerals, are removed in solution from the site of weathering. The constituents in solution reflect the composition of the parent material and the physical and chemical conditions in the weathering environment. They remain in solution until the conditions in the secondary environment change and cause the precipitation of insoluble secondary minerals. Adsorption onto clays, Fe-, Al-, and Mn-oxides and organic matter can also remove soluble constituents from solution.

The products of weathering are dispersed in the surficial environment by biological and hydromorphic migration during soil formation, and the movement of ground and surface water and by mechanical means during erosion and transport of surficial material. The dispersion of the weathering products derived from mineral deposits results in the formation of secondary dispersion halos in the surficial environment. The dispersion halos comprise higher than normal concentrations of indicator elements which include target and pathfinder elements. Target elements are those that form the main components of economic interest in a given type of deposit.

Table 3.3. Secondary ore minerals formed in the zone of weathering. (From Peters, W.C. (1978), Exploration and mining geology, John Wiley and sons.

Ore Mineral Associations in the Zone of Oxidation, Excluding Supergene and Relict Sulfides (Minerals in italics are common; minerals in parentheses are resistates)

Element	Oxides	Carbonates	Silicates	Sulfates	Other
Aluminum	*"bauxite"* *gibbsite* *diaspore* *boehmite*				
Antimony	senarmontite cervantite valentinite = "antimony bloom"				
Arsenic	arsenolite = "arsenic bloom"				Arsenic *scorodite* (hydrous Fe-arsenate)
Beryllium			(*beryl*)		
Chromium	(*chromite*)				
Cobalt	cobaltian "wad"				*erythrite* (hydrous arsenate) = "cobalt bloom"
Copper	*cuprite* *tenorite* *"copper pitch"*	*malachite* *azurite*	*chrysocolla*	chalcanthite antlerite bronchantite linarite	*Copper* atacamite (halide) turquoise (phosphate)
Gold					(*Gold*)
Iron	*"limonite"* *goethite* *hematite* *lepidocrocite* (*magnetite*)	siderite	*nontronite*	*jarosite*	vivianite (phosphate)
Lead	minium = "red lead" massicot = "lead ocher" plattnerite	*cerussite*		*anglesite* plumbojarosite	*wulfenite* (molybdate) vanadinite (halide with V) pyromorphite (phosphate) mimetite (chlor-arsenate)
Manganese	*"wad"* *psilomelane* *pyrolusite* (hausmannite) (manganite)		(braunite)		
Mercury	montroydite				*Mercury* calomel (halide)
Molybdenum	*ferrimolybdite* ilsemannite				*powellite* (Ca-molybdate) *wulfenite* (Pb-molybdate)
Nickel			*garnierite*		*annabergite* (hydrous arsenate) = "nickel bloom"
Niobium-Tantalum	(niobite-tantalite)				
Platinum					(*Platinum*)
Rare Earths					
Silver				argentojarosite	(*Silver*) *cerargyrite*
Thorium	(*thorianite*)		(thorite)		(*monazite*) (Th-rare earth phosphate)
Tin	(*cassiterite*) = "wood tin" hydrocassiterite				
Titanium	(*rutile*) (ilmenite)				
Tungsten	tungstite				(*scheelite*) (Ca-tungstate)
Vanadium					vanadinite (halide with Pb) descloizite (complex vanadate) carnotite (K-vanadate)
Uranium	gummite *uraninite*		uranophane sklodovskite	uranopilite zippeite	autunite (Ca-phosphate) torbernite (Cu-phosphate) tyuyamunite (Ca-vanadate) *carnotite* (K-vanadate)
Zinc		*smithsonite* hydrozincite	*hemimorphite* = "calamine"	goslarite	
Zirconium			(zircon)		

Pathfinder elements are the elements in a mineral deposit or associated rocks which, by reason of differing properties (eg. mobility, ease or economy of analysis), may act as guides to mineralization. (Butt and Smith, 1979). The chemical mobility of the elements involved will affect the behaviour of the elements during dispersion and, thus, control the type of dispersion halo formed, the size and shape of the dispersion haol, the anomaly contrast and the extractability of the anomalous elements in the surficial material.

Mobile elements are those elements which are partitioned to natural waters during weathering and can thus be easily dispersed from the site of weathering. The relative mobility of elements depends on their mode of occurrence in natural waters. Elements which form stable solutes and suspensoids in water, or occur as components that do not react rapidly, will be most mobile. Those that occur as less stable forms in water, such as ionic constituents, tend to be more easily precipitated by immobile phases and, thus have a lower effective mobility. The highly mobile elements will tend to be removed from the weathering environment, while less mobile elements are precipitated at various distances from the source and form hydromorphic anomalies in soils and stream sediments.

Immobilized elements (Butt and Smith, 1979) are those elements bound in solid phases which are limited to mechanical dispersion. They include elements in resistant primary minerals, elements forming major components of secondary minerals, elements which form minor components of secondary minerals (eg. incorporated in clay lattices or co-precipitated with Fe-oxides) and elements incorporated in organic matter.

The chemical mobility of elements in the surficial environment, and consequently their hydromorphic dispersion, varies considerably from one location to another. The factors affecting the aqueous migration of elements in the surficial environment are discussed by Rose, Hawkes and Webb (1979, Chapter 8) and by Beus and Grigorian (1977, pp 41 - 47). The major factors which should be evaluated during orientation studies in order to interpret geochemical surveys in a particular environment are summarized below.

a) <u>pH and Eh values of surficial environments</u>.

The pH and Eh of water in the surficial environment are largely responsible for the mobility of elements and their differentiation during transport. Acid or weakly acid waters with a pH of less than 6 are particularly favourable for the migration of many trace elements found in mineral deposits. The strongly acid solutions formed during the weathering of sulphide deposits are capable of transporting elements which are normally only weakly mobile. The distances over which the elements are transported depends on the rate at which solutions are neutralized by the material through which they migrate. Metallic elements can be precipitated as oxides and hydroxides by increasing the pH. The pH of precipitation of many transition elements occurs within the pH range of natural waters (Fig. 3.3), while the pH of precipitation of alkali and many alkali-earth elements is above the natural range.

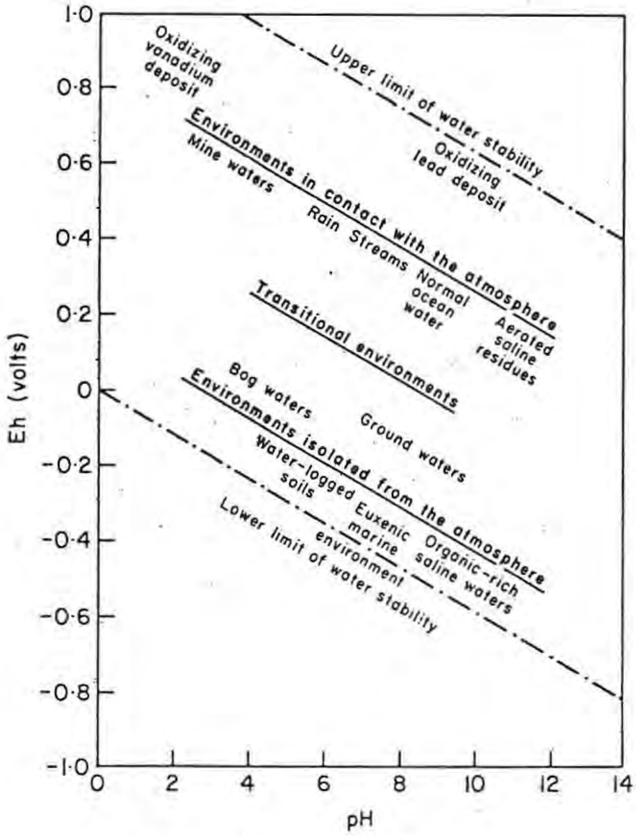


Fig. 3.3. Approximate position of some natural environments as characterized Eh and pH. From Rose, Hawkes and Webb (1979).

The oxidation - reduction potential, which refers to the concentration of electrons in the environment, affects the valence state of elements.

Eh is a convenient measure of the oxidation - reduction potential. The properties (eg. solubility) of elements with more than one valence state change considerably with a change in valence state. Eh thus has an important effect on the mobility of some elements (eg. Fe^{2+} and Fe^{3+}) in the surficial environment.

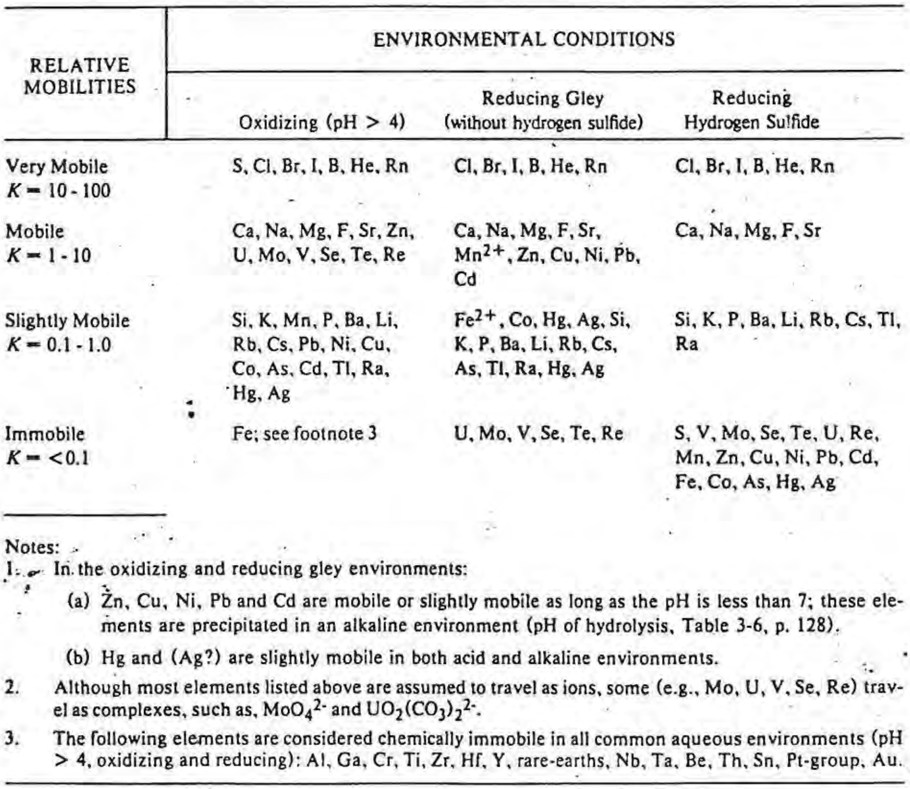
The relative mobilities of elements in the surficial environment, based on Eh and pH, is shown in Fig. 3.4. The classification is, however, only an approximation as a number of other factors will affect the mobility of elements in the aqueous phases of various environments.

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

Fig. 3.4. Relative mobilities of the elements in the surficial environment. From Levinson (1974).

b) The presence of precipitation agents.

The ability of a solution to oxidize or reduce ions depends on the presence of constituents such as free oxygen, organic compounds, hydrogen sulphide, ions of ferric and ferrous iron, and bivalent and tetravalent manganese. These constituents tend to control the course of oxidizing - reducing reactions and thus affect the mobility of many elements. The abundance and form of C and S in solution, which are in turn dependent on the pH and Eh of the environment, control the mobility of many elements by the formation of insoluble compounds. The presence or absence of hydrogen sulphide in reducing has a marked effect on the relative mobility of many elements (Fig. 3.5).



RELATIVE MOBILITIES	ENVIRONMENTAL CONDITIONS		
	Oxidizing (pH > 4)	Reducing Gley (without hydrogen sulfide)	Reducing Hydrogen Sulfide
Very Mobile $K = 10 - 100$	S, Cl, Br, I, B, He, Rn	Cl, Br, I, B, He, Rn	Cl, Br, I, B, He, Rn
Mobile $K = 1 - 10$	Ca, Na, Mg, F, Sr, Zn, U, Mo, V, Se, Te, Re	Ca, Na, Mg, F, Sr, Mn^{2+}, Zn, Cu, Ni, Pb, Cd	Ca, Na, Mg, F, Sr
Slightly Mobile $K = 0.1 - 1.0$	Si, K, Mn, P, Ba, Li, Rb, Cs, Pb, Ni, Cu, Co, As, Cd, Tl, Ra, Hg, Ag	Fe^{2+}, Co, Hg, Ag, Si, K, P, Ba, Li, Rb, Cs, As, Tl, Ra, Hg, Ag	Si, K, P, Ba, Li, Rb, Cs, Tl, Ra
Immobile $K = <0.1$	Fe; see footnote 3	U, Mo, V, Se, Te, Re	S, V, Mo, Se, Te, U, Re, Mn, Zn, Cu, Ni, Pb, Cd, Fe, Co, As, Hg, Ag

Notes:

1. In the oxidizing and reducing gley environments:
   (a) Zn, Cu, Ni, Pb and Cd are mobile or slightly mobile as long as the pH is less than 7; these elements are precipitated in an alkaline environment (pH of hydrolysis, Table 3-6, p. 128).
   (b) Hg and (Ag?) are slightly mobile in both acid and alkaline environments.
2. Although most elements listed above are assumed to travel as ions, some (e.g., Mo, U, V, Se, Re) travel as complexes, such as, MoO_4^{2-} and $UO_2(CO_3)_2^{2-}$.
3. The following elements are considered chemically immobile in all common aqueous environments (pH > 4, oxidizing and reducing): Al, Ga, Cr, Ti, Zr, Hf, Y, rare-earths, Nb, Ta, Be, Th, Sn, Pt-group, Au.

Fig. 3.5. Relative aqueous mobilities of selected elements in the surficial environment. From Levinson (1980).

c) The formation of complexes.

The mobility of elements may be increased in certain environments (eg. Zn and Pb in alkaline solutions) by the formation of mobile complexes with other elements or radicals. A wide variety of complex hydroxy - and oxy -ions are formed in alkaline solutions by metallic elements. Beus and Grigorian (1977) suggest that solutions in the supergene zone exhibit widespread complexing and that the complexes generally favour the solubility of metals. The effect of ionic mobility are considered to be of lesser importance.

d) Adsorption and ion exchange on colloidal particles.

Iron, aluminium and manganese oxides and hydroxides, organic matter, clays and silica are the most common natural materials occuring as colloidal particles. The small particles can adsorb significant amounts of trace element ions from solutions. The adsorbed ions may move into the lattice sites of the particles by ion exchange. Scavenged elements are immobilized in soil and stream sediments by flocculation of the colloidal particles. The mobility of the trace element is, thus, controlled by the behaviour of the sorbent and not by the concentration in the solution of the element being adsorbed. Highly mobile elements (see Figs. 3.4 and 3.5) may be precipitated in this way, while immobile elements, which are only slightly soluble, may be concentrated in certain enviroments. The adsorbed elements are generally weakly bonded and are readily extractable in weak aqueous reagents.

e) Organic matter.

Organic matter occurs in all soils, stream sediments and natural waters and can be a major constituent of the materials in some environments. Simple organic compounds and humic substances, even in small amount, can have important effects on the chemistry of trace elements. The effects include the complexing of trace ions by dissolved organic matter resulting in increased mobility of the elements. Organo-metallic complexes (chelates) can be formed in the surficial environment and many of these chelates are soluble. The chelates which migrate in soils are readily assimilated by plants and contribute to the distribution of elements by biological factors. Adsorption or formation of insoluble organic compounds can immobilize some elements. Reduction of elements to lower valence states by organic matter results in changes in the chemical properties of the elements and affects their mobility.

The chemical mobility of elements has a major effect on their mechanical and biological dispersion due to the interaction of the mobile aqueous phase with immobile and mobile clastic phases in the surficial environment (Fig. 3.6). The dispersion of elements by mechanical, hydromorphic and biological factors during soil formation, groundwater movement, and erosion and transport of surficial material, as well as the characteristic dispersion halos which are formed, are discussed in the following sections.

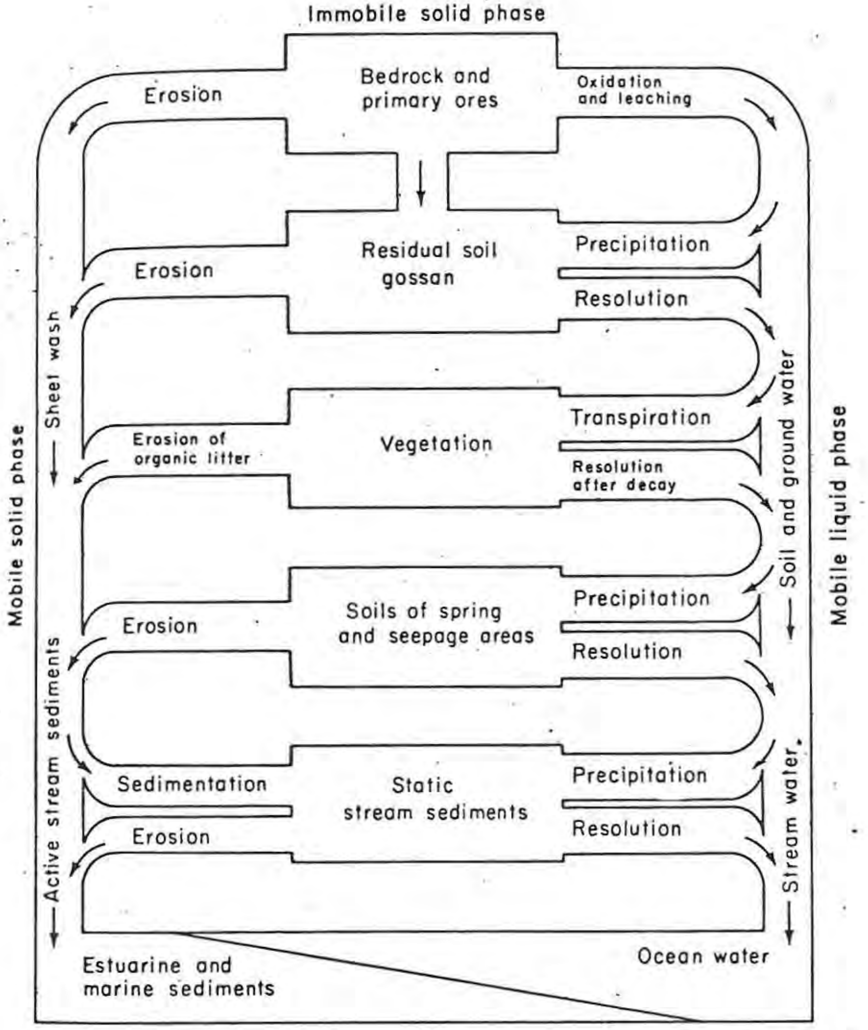


Fig. 3.6. The dispersion of weathering products. The diagram illustrates the interaction of mobile liquid and solid phases, immobile solid phases during the hydromorphic, mechanical and biological dispersion of elements in the surficial environment. From Rose, Hawkes and Webb (1979).

3.1.4. Residual soil profiles, gossans and residual anomalies.

Residual surficial material is characterized by the organization of its constuents and properties into layers related to the daylight surface. The layering grades upwards from weathered bedrock, in which the residual and insoluble products of weathering are essentially in situ, to the near surface zones where the weathering products are redistributed by the process of soil formation. The soil forming process (Fig. 3.7) is essentially a continuation of the weathering process with the addition of biologic activity, vertical transfer of material and removal of some constituents. The processes responsible for the developement of soil profiles are discussed by Birkeland, 1974 (pp 103 - 122). The formation of soil profiles can only take place in areas where the rate of erosion is less than the supply of material and the rate of soil-formation.

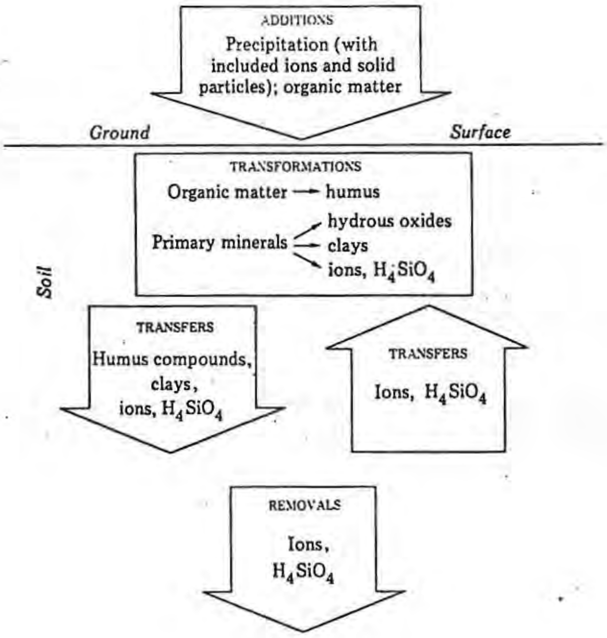


Fig. 3.7. A flow chart of the major processes of soil profile development. From Birkeland (1974).

The zone of weathering, below the level of biologic activity, consists of parent material in various stages of decomposition. The deepest horizon (Fig. 3.8) comprises essentially solid bedrock, of variable thickness, which is discoloured by Fe oxides and in which incipient alteration of silicate minerals to clays can be seen. The incipient decomposition is concentrated along joints and fractures, with the extent of alteration gradually increasing upwards from fresh parent material. Bedrock which has been exposed to long periods of deep weathering may be completely altered to secondary minerals, generally clays, while still retaining the original bedrock structures. This chemically altered, but coherent, in situ material is referred to as saprolite. The soluble constituents of the saprolite are entirely leached, with a resultant relative accumulation of insoluble constituents and resistant primary minerals. The weathered bedrock, or saprolite if it is developed, grades into a horizon of weathering products in which the original rock structures are disturbed. The horizon is not significantly affected by biologic activity and may be the site of absolute enrichment of weathered material by the precipitation of iron oxides, silica or calcium carbonate in suitable environments.

The weathered profile developed over various types of sulphide deposits results from the decreasing effect of oxidizing ground water with depth. The profile developed is largely dependent on the climate, the depth and fluctuation of the water table, the physico-chemical nature of the ore and host rock, and on the local and regional geomorphology. The complex interplay, over time, of these factors results in the formation of widely different sulphide-oxide profiles which may include all or some of the zones indicated in Fig. 3.1 and Table 3.1.

Gossan - massive limonitic and jaspilitic capping.

Oxide zone - characterized by leaching of mobile elements in the upper portions and the formation of secondary minerals at deeper levels where oxide enrichment may take place.

Supergene Sulphide zone - the reducing environment below the water table can be characterized by secondary sulphide enrichment due to introduction of metals leached from the oxide zone.

Transition zone - characterized by the incipient alteration of primary ore minerals.

Primary ore - unweathered parent material.

Blain and Andrew (1977) compiled a series of type profiles, based on a review of the principle massive sulphide ore associations, which can be used as a basic guide to the various types of sulphide-oxide profiles.

Ironstone are an important feature of weathered profiles, as deeply weathered massive and disseminated sulphide deposits are commonly represented by leached jaspilitic gossan or by iron-rich oxide assemblages which bear little resemblance to the primary deposit. Ironstone may, however, be developed from a wide range of lithologies by physical and chemical convergence during weathering. (Andrew, 1978, pp 5) The field relationships, as well as mineralogical and textural features of ironstones, can often be used to recognize gossans related to sulphide deposits, as opposed to in situ and transported ironstones derived from unmineralized rocks (Blanchard, 1968). The major and trace element geochemistry of ironstones can be used to:

a) distinguish gossans from other ironstones in deeply weathered profiles where saprolites and laterites are present (eg. Western Australia)

b) recognize gossans where field relationships and textural features are not diagnostic

c) distinguish between gossans derived from pyrite/pyrrhotite deposits and those derived from sulphide deposits containing significant base metal mineralization.

The geochemical evaluation of gossans can be based on quantitative techniques (e.g. Moeskops, 1977) and is far less subjective than evaluation based on physical and textural criteria. The interpretation of ironstone geochemical surveys, however, has to be based on orientation surveys as the geochemical characteristics of gossans and ironstones are highly variable on both regional and local scales. The orientation surveys should investigate the trace element geochemistry of various types of ironstones in the area of interest, particulary gossans associated with known mineralization, in order to select a suite of elements which characterize specific types of ironstones. Easily determined elements which can differentiate true gossans should be used in routine surveys (e.g. the target elements), with the other trace elements only determined in uncertain cases (Moeskops, 1977). The major element geochemistry of ironstones is not diagnostic of the parent material, but the relationships between major and trace elements can be important aids in the interpretation of ironstone geochemical surveys. The relationships which should be considered include:

a) High silica content indicates dilution of the Fe content and tends to reduce the trace element content.

b) A high Al content is indicative of the presence of clay minerals which can adsorb trace elements.

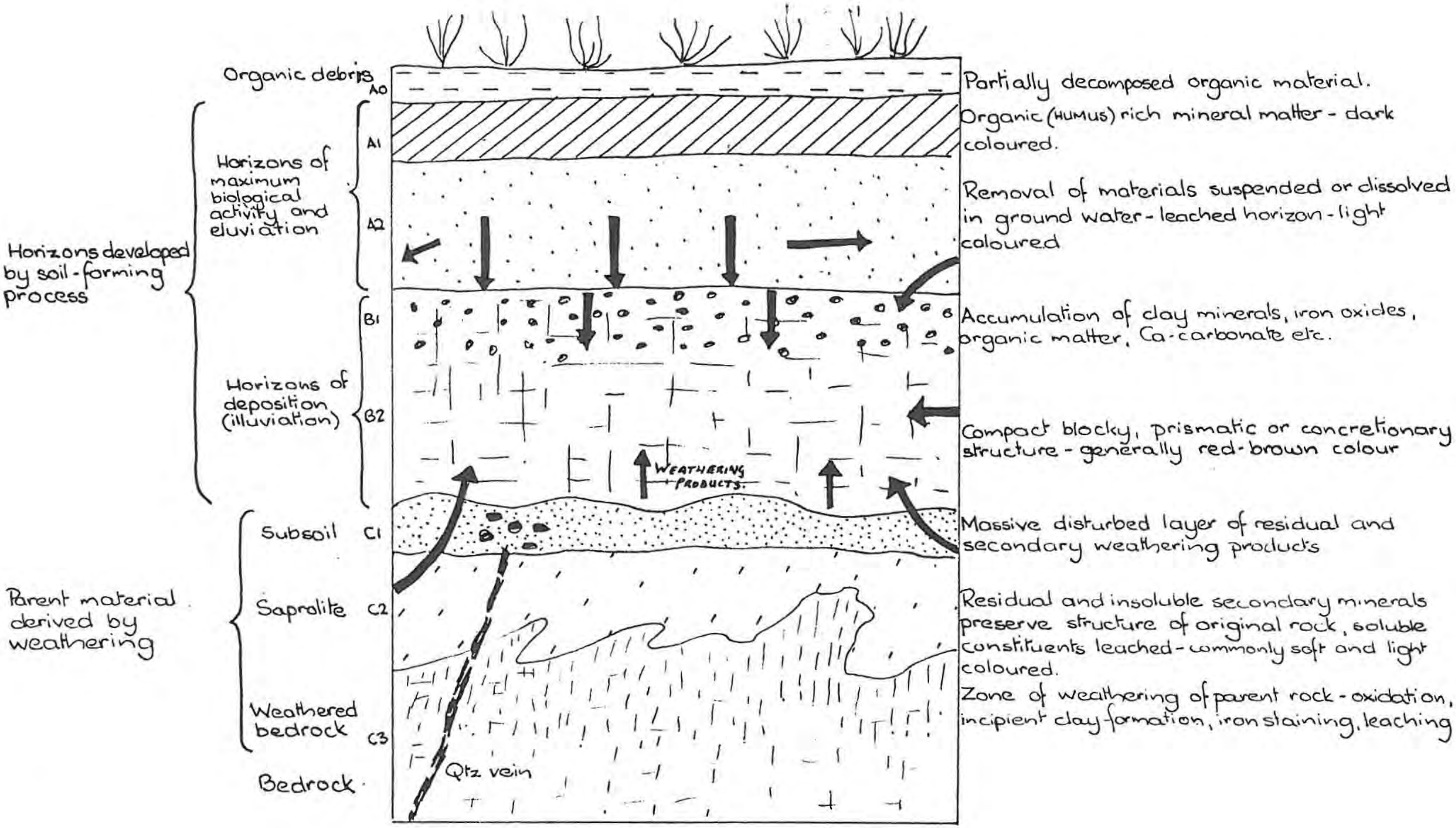


Fig. 3.8. Generalized mature soil profile showing the soil horizons commonly developed in warm, humid climates.

c) The coincidence of high Mn and trace element contents is often indicative of scavenging by manganese hydroxides, whereas true gossans are often characterized by high Fe and coincident trace element concentrations.

Ironstone and gossans, including their geochemical characteristics and other features affecting exploration, are discussed by Blanchard (1968), Blain and Andrew (1977) and Friggins (1979).

The upper horizons of a mature soil profile have well developed layering and show the least correlation with the parent material. The A horizon (Fig. 3.8) is characterized by the accumulation of organic matter near the surface. The decaying organic-matter (humus) lowers the pH of vadose water percolating downwards through the soil. The acidic groundwater leaches the soluble components and eluviates clay and humus from the lower portion of the A horizon forming a characteristically light coloured layer. The B horizon is characterized by illuviation which results in the accumulation of clay, iron oxides and fine grained organic matter. The B horizon has a characteristic compact structure, is generally dark brown-red in colour and may be concretionary.

The weathering products from mineral deposits are dispersed in residual soil profiles where they form syngenetic geochemical anomalies directly overlying the mineral deposit. The anomalies are a reliable, direct and straight forward guide to buried mineralization as the primary geochemical pattern is generally expressed in a recognizable fashion. The interpretation of residual secondary dispersion patterns is, however, complicated by the behaviour of the target and pathfinder elements during the dynamic processes taking place in the surficial environment. The behaviour of the elements is largely related to their mobility and effects the following characteristics of the syngenetic anomalies in residual soils:

a) The mode of occurrence of the target and pathfinder elements.

Immobile elements are incorporated in the coarser fractions of residual soil materials as components of resistant primary minerals and stable secondary ore minerals. The mobile and semi-mobile elements tend to be leached from the soil profiles and are only retained as firmly bonded minor components of clays and hydrous Fe- and Mn-oxides. They are thus concentrated in the finer fractions of the soils. The residual soil anomalies are characterized by relatively strong bonding of the indicator elements.

b) The intensity and contrast of anomalies.

The range of trace and minor elements generally encountered in soils derived from common parent materials is shown in Figure 3.9. The ranges indicated are, however, only a guide as the trace element content of soils is dependent on the element abundances in the parent material and on the effects of the weathering and soil-forming processes. The intensity and contrast of syngenetic soil anomalies will tend to reflect the contrast between the mineral deposit and the country rocks. Factors related to the mineral deposit (e.g. the mineralogy and grade of the deposit, the degree of oxidation and leaching of the sub-outcrop, variations in the composition and permeability of the wall-rock lithology, etc.) and factors related to the surficial environment (e.g. the type, depth and maturity of soil profiles, topography, drainage, climate, etc.)cause variations in the intensity and contrast of the anomalies. Orientation studies must thus be carried out to establish the characteristic intensity and contrast of anomalies related to mineral deposits in the exploration area in order to recognize significant anomalies.

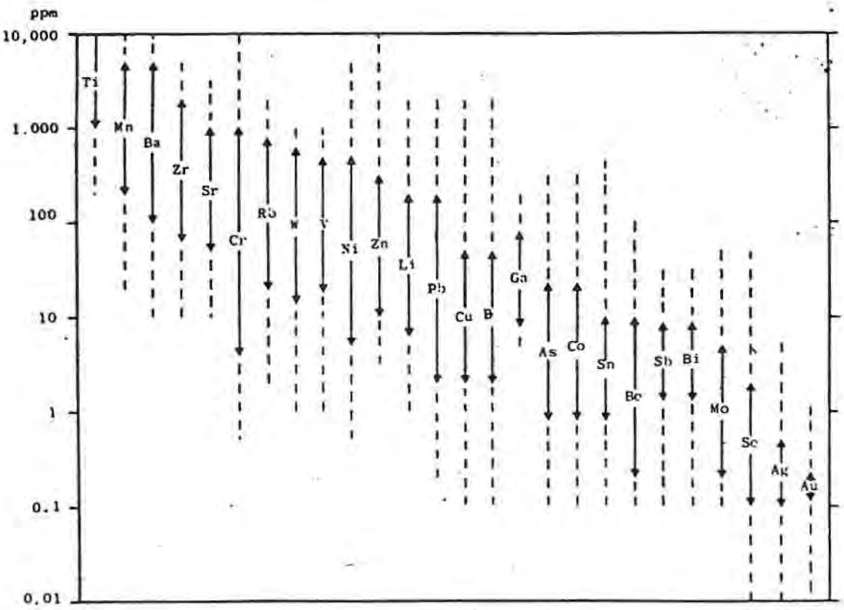


Fig. 3.9. Range of abundance of trace elements commonly found in soils. Dashed lines indicate more unusual values. From Levinson (1974).

c) The variation of trace element content with depth.

Background and anomalous contents of elements vary with depth in the soil profile due to partitioning of weathering products into various horizons by soil forming processes. The distribution of elements is dependent on the physical and chemical properties of the soil profile (e.g. Fig. 3.10) and on the mobility of the target and pathfinder elements. The distribution of elements in soil profiles is largely a function of local conditions and generalizations about the distribution of a particular element in any soil type can be misleading. Orientation studies should be used to determine the distribution of elements in soils in an exploration area in order to select the optimum horizon for sampling. The variation of elements with depth in the soil profile can complicate the interpretation of geochemical soil surveys if care is not taken to sample from a constant soil horizon.

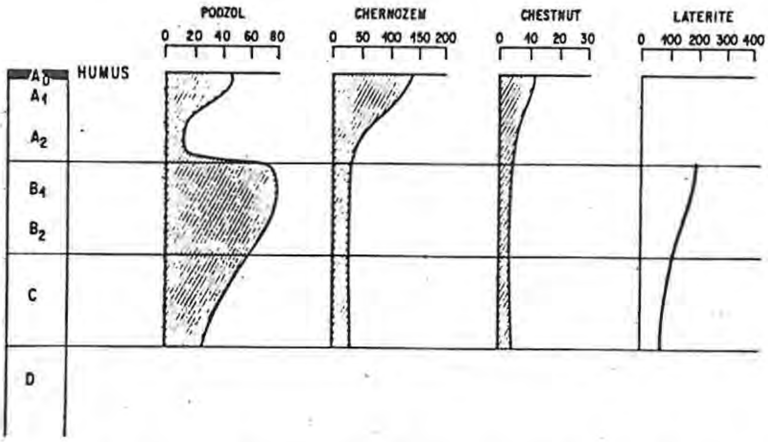


Fig.3.10 Generalized representation of the distribution of copper in four different types of soil. Distributions for podzol, chernozem and chestnut soils are based on data from the Soviet Union (Vinogradov, 1959). The laterite distribution is based on data from Zeissink (1971). In the laterite profile, insufficient information is available for the A horizon to permit generalizations. All values in ppm.

From Levinson (1976).

d) <u>The lateral extent of residual soil anomalies.</u>

The lateral extent and shape of residual soil anomalies reflects the original size of the primary geochemical pattern related to the mineral deposit, plus the effects of secondary dispersion. Residual anomalies in flat areas reflect the shape of the primary dispersion pattern. The C horizon generally shows limited dispersion, although chemical dispersion in the zone of weathering can be significant under favourable conditions (e.g. Scott, 1975, in Rose, Hawkes and Webb, 1979, pp 274). Dispersion in the A and B horizons of the soil profile is caused by normal soil forming processes, by groundwater movement, by mechanical factors such as soil compaction and soil creep and by biological factors. The residual anomalies in the upper zones of the soil profile will thus tend to be larger than the primary geochemical halos. (Fig. 3.1) The actual amount of dispersion in the soil profile is a function of local conditions and the mobility of particular elements under those conditions. Dispersion tends to decrease the intensity of residual geochemical anomalies.

e) Distortion of residual anomalies by denudational processes.

Relief has a major affect on the lateral extent of anomalies due to increased mechanical and hydromorphic dispersion. Dispersion halos in soils will only be located directly above mineral deposits in flat areas where residual soil is essentially in situ. Soils derived from the weathered bedrock will tend to be transported down slopes by the denudational processes responsible for the development of landforms (Corbett, 1978). The denudational processes affect the surface layers of surficial material over large areas of hill slopes, and differ from the processes of erosion which are confined to linear drainage courses. The main processes of denudation are surface wash by the run-off of excess precipitation and gravitational processes such as soil creep and solifluction as well as rapid flow, slip or free fall of surficial material. The dispersion caused by surface wash generally only involves the selective removal of material from the surface of residual soil. The gravitational processes involve mass movement of unconsolidated material and can have a profound affect on the characteristics of secondary geochemical halos, particularly residual soil anomalies.

The recognition of soils transported by denudational processes is often difficult, but for reconaissance purposes most soils derived from bedrock can be considered as essentially in situ. Soils derived from overburden of remove origin (e.g. alluvial, glacial and aeolian overburden) pose serious problems for the interpretation of geochemical surveys. The interpretation of detailed soil surveys should, however, always be based on an investigation of the local soil profiles and landforms in order to anticipate the effects of denudational processes on geochemical anomalies. The nature and developement of landforms is reviewed by Corbett (1978) and the effects of mechanical dispersion by denudational processes on residual anomalies is illustrated by Rose, Hawkes and Webb (1979, Chapter 9).

f) The homogeneity of residual anomalies.

The homogeneity of residual anomalies in mature soils depends largely on the grain size and distribution of the constituents containing the indicator elements. Discrete grains of resistant primary or secondary minerals tend to give irregular anomalies, while a more regular distribution is characteristic of anomalous constituents associated with finer grained material (e.g. clays, hydrous oxides) which are normally more evenly distributed in soil horizons. The distribution of the indicator elements in the bedrock may be the major control on the homogeneity of anomalies in immature soils.

The type of soil profile developed in an area is a function of five major factors which interact to cause variations in the idealized profile in Fig. 3.8. The factors, which are discussed by Birkeland, 1974, are:

a) Climate - particularly rainfall and temperature.
b) Organisms - vegetation and animals.
c) Topography - relief, landforms and drainage.
d) Parent material - bedrock, weathered rock and transported overburden.
e) Time - including tectonic and climatic changes.

The regional balance between the factors defines physiographic provinces with diagnostic trends in weathering and soil formation. Local variations within a region are, however, responsible for a range of weathering profiles and soil types having different properties and chemical characteristics which affect the characteristics of secondary dispersion halos. Classification and mapping of local soil types and profiles based on the characteristics, such as colour, texture, composition, content of organic matter, trace element distribution, structure bulk density, permeability and porosity, cation exchange capacity and soil pH, of the various soil horizons is essential for the interpretation of detailed soil geochemical surveys. General descriptions of soil classification, genesis and characteristics are given by Birkeland (1974) and Hunt (1972). The classification of South African soils is described by Macvicar and de Villiers (1977) and the principles involved in field studies of soils are described by Clarke and Beckett (1971).

3.1.5. Ground water in the surficial environment and hydromorphic anomalies.

Ground and surface water, derived mainly from precipitation, is an important component of the surficial environment. The various classes of water in the surficial environment and their relative movements are illustrated

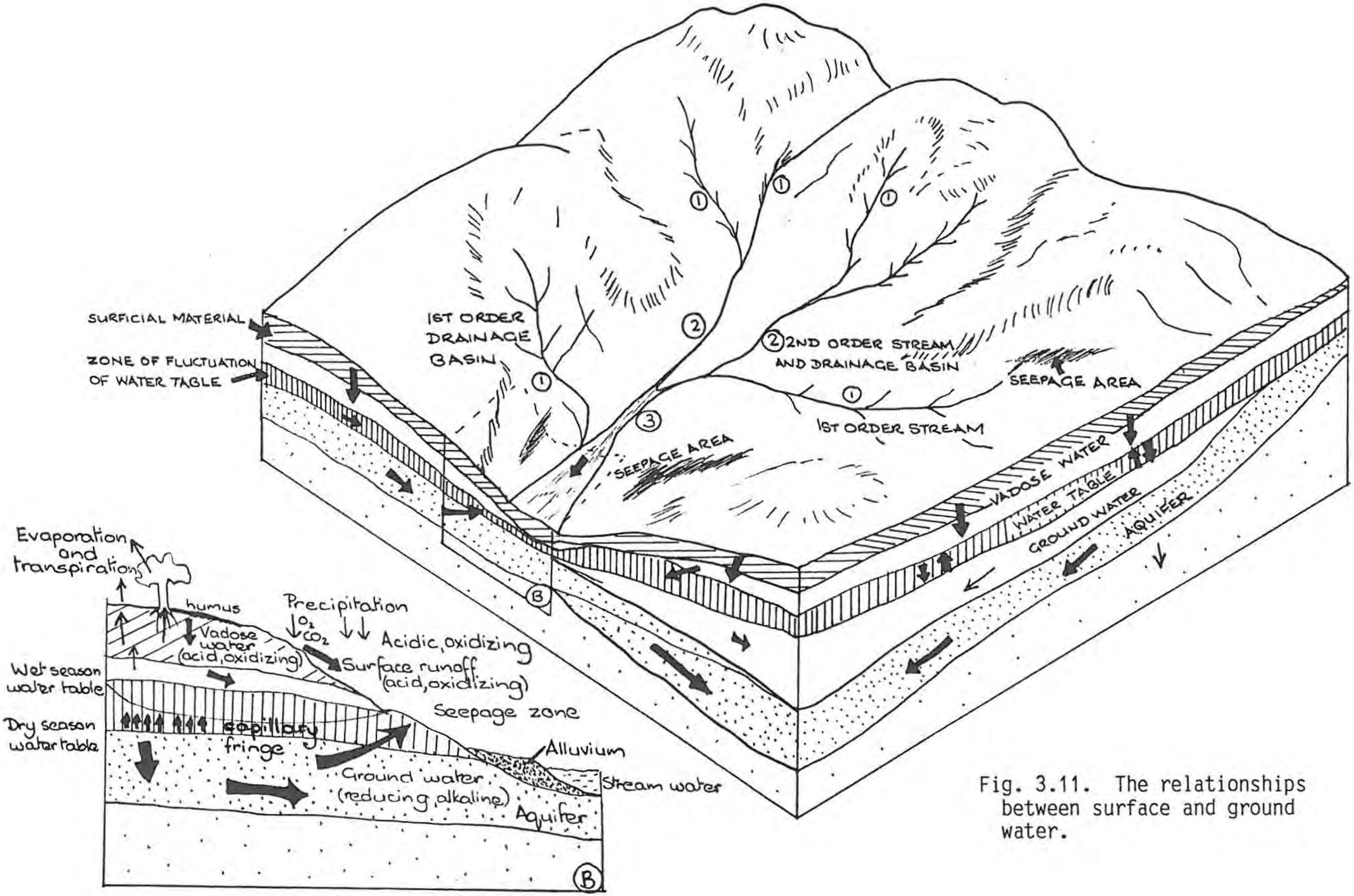


Fig. 3.11. The relationships between surface and ground water.

in (Fig. 3.11). Surface water which plays a major role in the denudation, erosion and transport of surficial material is discussed in the sections on transported and drainage anomalies. The effect of ground water on the processes of weathering and soil formation has already been indicated. The soluble products liberated during these processes are transported by ground water and hydro-geochemical anomalies are caused by concentrations of mobile elements in ground water in the vicinity of weathering mineral deposits. The mobile elements are precipitated by changes in the chemical environment (e.g. seepage areas) where they form bonded epigenetic anomalies.

The water-table is the upper limit of completely saturated lithospheric material and forms a subdued reflection of the topography. The depth of the water-table varies according to local conditions and it may occur near the surface in wet, poorly drained areas or it may be hundreds of feet deep in arid areas. Seasonal variations in supply and recharge by precipitation results in fluctuations of the water-table. The height of the water-table and the precipitation - evaporation ratios in an area affect the development of soil profiles (Fig. 3.12), as well as the leaching and precipitation of mobile trace elements in the surficial environment.

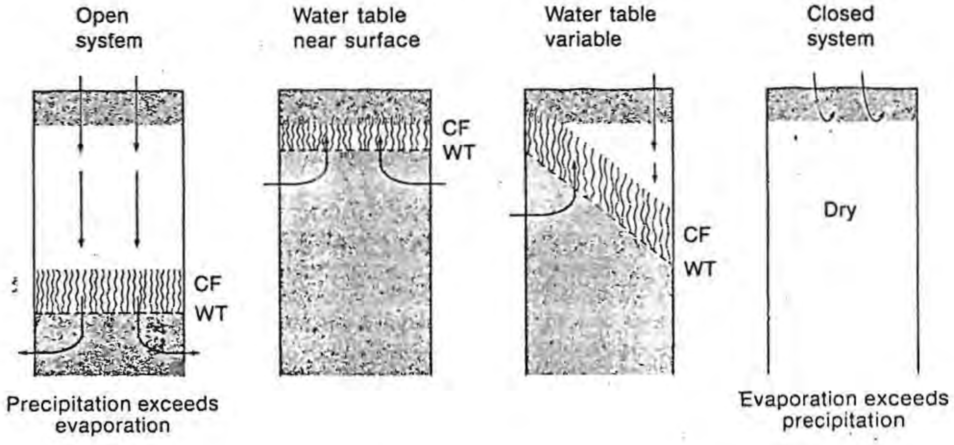


Fig. 3.12. Water regimes, which affect soil development are controlled partly by the precipitation-evaporation ratio and partly by the height of the water table (WT) and capillary fringe (CF). Direction of water movement is shown by arrows. At the two extremes are the open and closed systems that form, respectively, acid and alkaline soils. Conditions are mixed where water tables are sufficiently shallow for the capillary fringe to moisten the soil or where the height of the water table fluctuates seasonally. From Hunt (1972).

Vadose water, which occurs in the zone of aeration between the water-table and the surface, tends to be oxidizing and acidic due to the presence of dissolved oxygen, carbon dioxide and humic acids from the atmosphere and the soil profile. The acidic water, particularly near weathering sulphide deposits, tends to leach mobile elements from the weathering products and to cause their redistribution by vertical movement. Residual soil anomalies may be re-inforced by the evaporation of ground water and the precipitation of mobile elements. Plants use vadose water from the soil and accumulate trace elements from the water by transpiration. The accumulated elements in plants are added to the soil by decomposition of plant material. During wet periods the vadose water, together with dissolved mobile elements, moves through the soil profile to recharge the water-table.

The movement of ground water below the water-table is related to the hydraulic gradient and to the permeability of the rocks and tends to be slow. Surficial material and permeable sedimentary rocks are good acquifers. Crystalline igneous and metamorphic rocks have low porosity and their permeability is largely due to interconnected joints and fractures. The ground water tends to be reducing and alkaline, but the pH and Eh of the water, as well as the trace element content, can vary depending on the composition and reactivity of the material through which it moves.

Ground water moving away from mineral deposits can contain anomalous concentrations of mobile elements. The extent, intensity and contrast of the hydrogeochemical anomalies is largely dependent on the mobility of the elements in the deposit and on the physico-chemical characteristics of the gound water. The dominant factor affecting the mobile element content of ground water is pH, which is strongly influenced by bedrock composition. Water moving through carbonate rocks will tend to be neutral to alkaline, limiting the mobility of elements and the extent of hydromorphic anomalies. Igneous rocks, on the other hand, have little effect on the pH of the ground water resulting in greater mobility of elements. The mobile elements tend to remain in solution and be transported until the ground water passes into a different chemical environment with a resultant accelerated precipitation of insoluble compounds. Ground water up-drainage from the precipitation barrier will contain hydromorphic anomalies, while below the barrier anomalous elements will be associated with clastic material.

Seepage areas, where the ground water moves to the surface, are important precipitation barriers. The seepage areas generally occur along the break - in - slope of surface drainage basins and are commonly the site of epigenetic anomalies in soils, in vlei sediments and in the seepage muck of springs. The form and location of seepage anomalies is, however, controlled by the local relationships between relief and the water-table. The elements in seepage anomalies occur as components of precipitated hydrous oxides and as readily soluble components of the fine-grained fraction of the surficial material. Organic matter and clays in seepage areas of poorly drained soils are important adsorbents of mobile elements. The elements present in seepage anomalies and the intensity and contrast of the anomalies is dependent on the mobility of the target and pathfinder elements in the local surficial environment

The large amounts of organic matter accumulated in bogs and swamps is an important precipitation barrier. Mobile elements contained in ground and surface-water tend to be accumulated in bogs and swamps. The pH and Eh of bogs and swamps have complex vertical and lateral patterns which cause variations in trace elements accumulated in various parts of the swamp. The major consideration is that bogs and swamps normally have much higher mobile element contents than surficial material and will appear anomalous in relation to other drainage sediments or to surrounding soils.

3.1.6. Geochemical dispersion patterns in drainage systems.

Primary geochemical patterns are reflected in drainage systems by mechanical and hydromorphic dispersion of weathering products in the catchment areas. The processes of denudation and erosion supply clastic material to the streams from the surficial environment of the catchment areas. The clastic material is transported by traction, saltation and suspension in the streams. The active stream sediments may be temporarily or permanently immobilized by deposition at various locations along the drainage system. Water, containing soluble weathering products, is supplied to the drainage systems by the surface run-off of excess precipitation and by a base-flow of ground water in areas with a shallow water-table. The soluble constituents may remain in solution and be hydromorphically dispersed in the drainage water, or they may be precipitated and added to the active or immobile sediments in the drainage system. Material from the catchment areas is, thus, firstly concentrated in the drainage systems and then dispersed down the drainage system. The characteristics of the disperion patterns formed are largely dependent on the balance between the mobile liquid phase, the active stream sediments and immobile material in the drainage systems. (Fig. 3.6)

Mineral deposits in the catchment areas of drainage systems are reflected by anomalous contents of mobile elements in water and by dispersion trains of anomalous sediments in favourable environments. The anomalous elements in active stream sediments are derived by the denudation, erosion and transport of anomalous clastic material from weathered mineral deposits, gossans, residual and transported soil anomalies, and hydromorphic anomalies in seepage sediments, and by the precipitation or adsorption of mobile elements in anomalous stream water. Anomalous elements in stream sediments may occur in the following clastic materials:

a) Resistant primary ore and gangue minerals which are generally dense and are, thus, concentrated in the heavy mineral fraction of stream sediments (e.g. cassiterite, wolframite, magnetite, garnet, etc.). Native metals (e.g. gold) and meta-stable ore minerals (e.g. sulphides) may also be present.

b) Secondary ore minerals, gossan fragments and other secondary weathering products containing immobile elements. The secondary minerals tend to be relatively friable and become finer grained down stream, resulting in winnowing and loss into the water.

c) Precipitates from stream water (e.g. insoluble trace minerals and Fe- and Mn-oxides) which commonly coat the surfaces of clastic grains or occur as very fine particles in suspension in the stream water. The trace minerals precipitated tend to remove mobile elements from solution and limit the extent of hydrochemical anomalies. Precipitation barriers, such as the mixing of stream waters of different pH, can cause false stream sediment anomalies.

d) Exchangeable elements adsorbed on Fe- and Mn-oxides, organic matter, clay particles, or other phases. This fraction readily equilibrates with the stream water and reflects the concentrations in the water at the sample site.

e) Organic material with incorporated indicator elements.

The relative proportions of the different types of anamalous constituents in the drainage sediments depend on the nature of the anomaly source and on the dispersion history of the sediments. The various types of anomalous constituents tend to be associated with different size and compositional fractions of the drainage sediments. The proportion of resistant primary and secondary minerals to hydromorphically derived constituents with weakly bonded indicator element affects the ease of extractability of the anomalous elements.

The stream sediment composition at a particular point in the drainage system represents a natural composite of the material in the catchment area upstream. The contrast and intensity of anomalies in the stream sediments depends on the contrast and intensity of the source anomalies and on the amount of dilution by material derived from barren sources. The maximum content of anomalous constituents generally occurs where ground water rich in indicator elements enters the drainage system or where streams intersect anomalous surficial material or mineral deposits. The indicator element content of the sediments or stream water falls fairly rapidly to background values above the point of entry of anomalous constituents. The recognition of the cut-off point is an important factor in the interpretation of drainage anomalies as the mineral deposit occurs up-drainage of the maximum anomalous values. Downstream of the entry point the content of anomalous constituents in sediments and water shows a progressive decline as a result of natural dilution.

The form of the downstream decay pattern of sediment anomalies is similar for anomalies of mechanical or hydromorphic origin. The principle factors affecting the persistence of a dispersion train are the contrast at the source, the input of indicator elements along the stream course and dilution by erosion of bank material and by confluence with barren streams. The characteristics of dispersion trains are also affected by unequal erosion rates in the drainage basin, resistance to erosion of various rock types and mineral deposits, the indicator element content of alluvial and colluvial bank material and the size of barren streams compared to anomalous streams. The effects of dilution may be reduced, and the length of detectable dispersion trains enhanced by separating barren material (e.g. quartz) from sediment samples. Dispersion of the different types of anomalous constituents (e.g. heavy mineral fraction or fine grained fraction) may vary and dispersion trains can be enhanced by concentrating certain fractions of the stream sediments.

The pH of stream waters, which effects the mobility of many elements, influences the characteristics and length of dispersion trains. The effect of pH is particularly important in limestone environments where the mobility of metals is reduced and dispersion trains are characteristically of limited extent. Dispersion trains may be further complicated by the scavenging and co-precipitation of indicator elements by iron, manganese and organic carbon. Elements leached from normal rocks, particularly in poorly drained areas with reduced pH and Eh, are concentrated in ground water and may cause false anomalies when precipitated by organic matter or hydrous iron and manganese oxides in more acidic and oxidizing stream waters. Anomalous concentrations of metals unrelated to mineral deposits are frequent occurrences in areas of impeded drainage.

The homogeneity of stream sediment anomalies is largely dependent on local differences in the grain size and mineralogy of the sediments and on the mode of occurence of the anomalous elements. Lateral variations in element content are caused by sorting of the sediments as a result of differential transport and deposition. Vertical inhomogeneity is caused by deposition of different types of material due to seasonal changes in stream velocity and the supply of anomalous and barren material.

Geochemical dispersion patterns in drainage systems are also reflected by the composition of stream and lake waters and lake sediments. The dispersion patterns in water and lake sediments are, however, more complex than those in active stream sediments. The use of hydrogeochemical and lake sediment geochemical surveys is only advisable where stream sediments cannot be successfully used (e.g. the glacially disorientated drainages of the Canadian Shield). Dispersion patterns in lake sediments and drainage water are described by Levinson (1974) and Rose, Hawkes and Webb (1979) and will not be considered in this dissertation.

3.2.0. Environmental Factors.

3.2.1. Geological factors as an environmental control and false geochemical anomalies.

The use of surficial material for geochemical exploration is based on the fact that secondary dispersion patterns reflect the primary geochemical patterns. However, features such as texture, porosity, permeability and the composition of rocks and mineral deposits affect the processes active in the surficial environment. Geological factors are, thus, an environmental control and the interpretation of secondary geochemical patterns can only be successful if the geology of the exploration area is taken into account.

Anomalous geochemical dispersion patterns in the surficial environment are often formed by features other than mineral deposits. Geological factors, such as rock units with significantly different concentrations of indicator elements, can cause apparent anomalies in the surficial environment (Fig. 3.13). Geochemical patterns unrelated to bedrock composition can be formed by environmental features such as changes in soil type, human activity, climate, relief and vegetation. The interpretation of secondary geochemical patterns requires an evaluation of the relative balance between geological and environmental factors affecting the geochemical landscape of an area, which requires an understanding of the geomorphology of an area, as well as the geology.

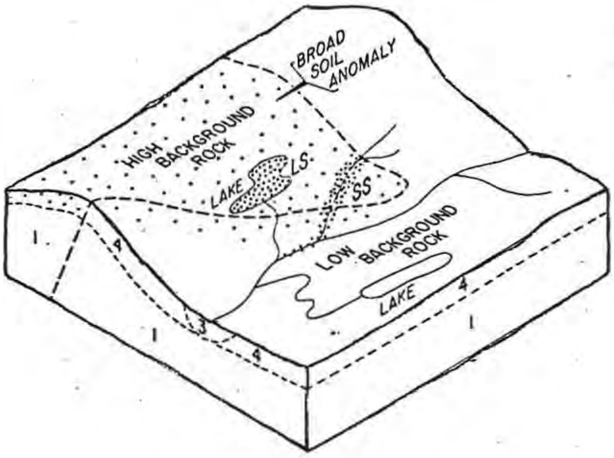
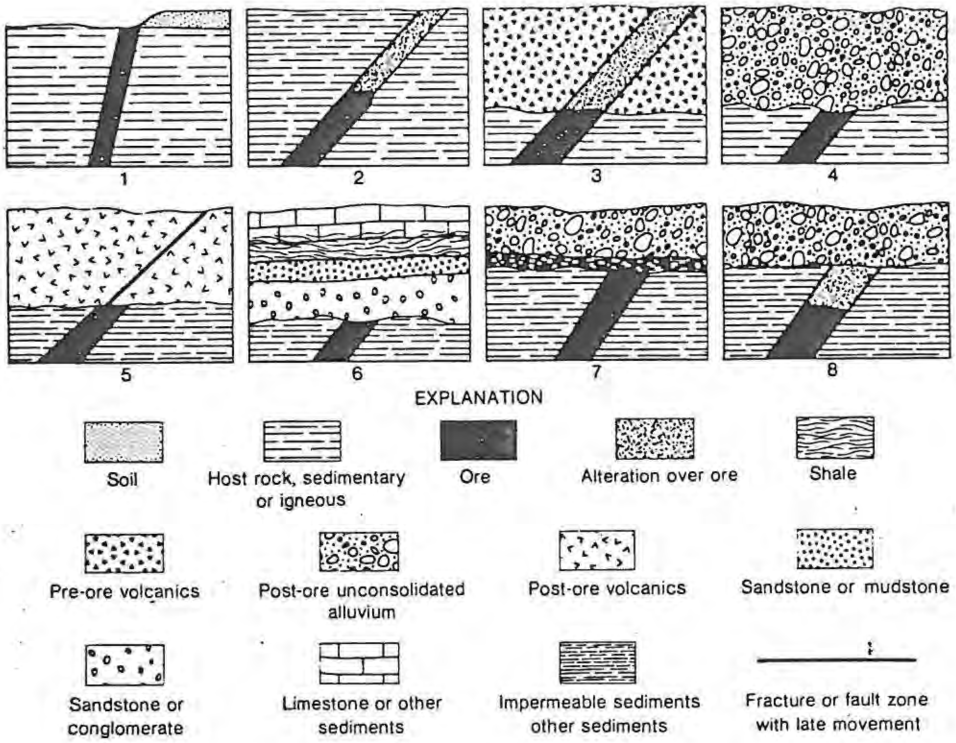


Fig. 3.13. Idealized model showing the effect of rock type change on the geochemistry of overlying soils and sediments. From Bradshaw (1975).

3.2.2. The position of mineral deposits and primary dispersion patterns relative to the surficial environment.

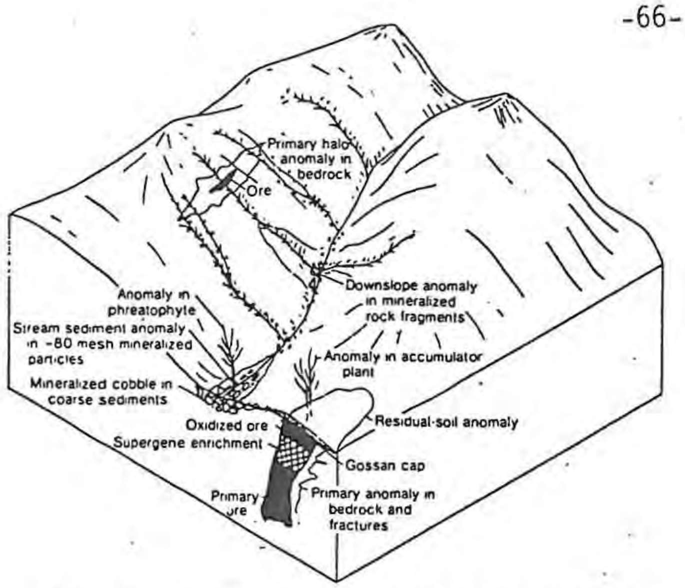
The processes operating in the surficial environment are limited to a relatively shallow zone of the lithosphere. The level of concealment of ore deposits and primary geochemical patterns during the evolution of the landscape and at the present time has a fundamental control on the secondary dispersion patterns related to the deposit.

Lovering and McCarthy (1978) compiled a series of generalized landscape geochemistry models which illustrate the increasing difficulty of locating deposits with increased complexity of concealment (Fig. 3.14). The models are based on case histories of geochemical exploration in the Basin and Range Province of the U.S.A. and only the basic concepts can be applied to other areas. The models do, however, indicate the interpretation of geochemical surveys should consider the tectonic and depositional history of the region being investigated. The tectonic history will indicate the level and complexity of concealment of mineral deposits likely to occur frequently within the area being evaluated.

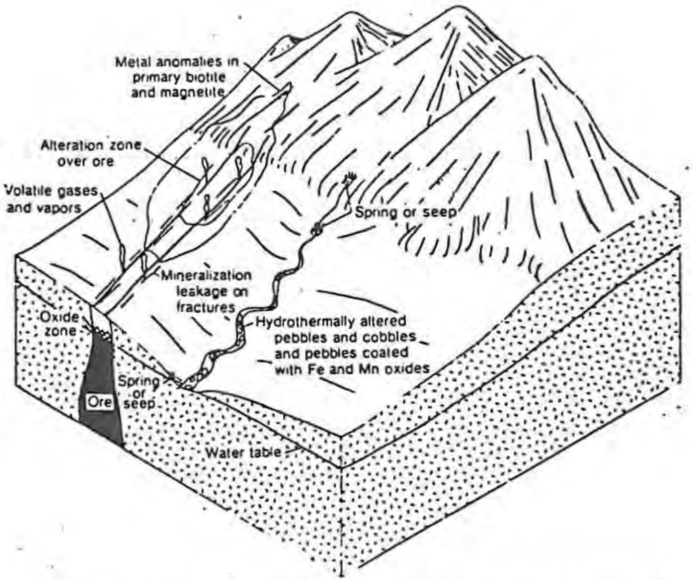


Sketch diagrams of ore targets, in order of increasing complication of concealment: 1 = outcropping mineralization, or concealed only by residual soil; 2 = alteration in host rock above mineralization; 3 = alteration in pre-ore volcanics overlying suboutcrop of mineralization; 4 = unconsolidated overburden over suboutcrop of mineralization; 5 = post-ore volcanics over suboutcrop of fault-controlled mineralization with post-volcanic movement along fault; 6 = unmineralized sedimentary rocks overlying mineralization; 7 = suboutcrop of mineralization beneath impermeable sediments; 8 = alteration in host rock over mineralization concealed beneath unconsolidated overburden.

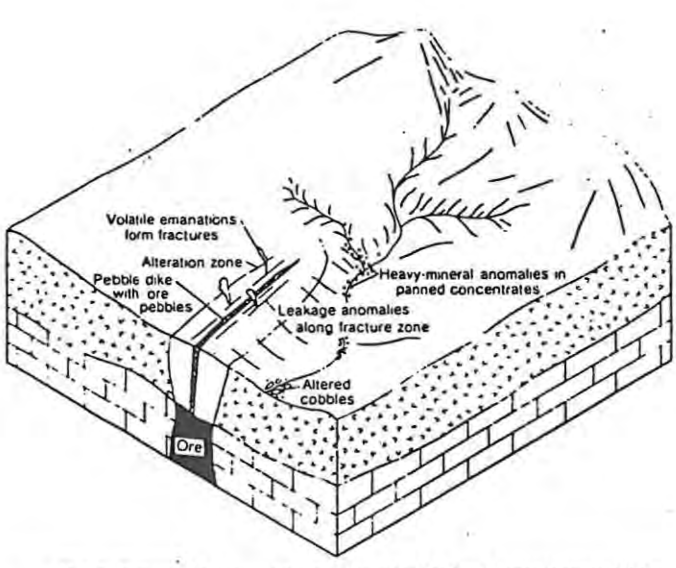
Fig. 3.14 A and B. Concealment of mineral deposits (A) and some conceptual geochemical models illustrating the geochemical halos which can be used to locate outcropping and buried mineral deposits (Fig. 3.14 B, next page). From Lovering and McCarthy (1978).



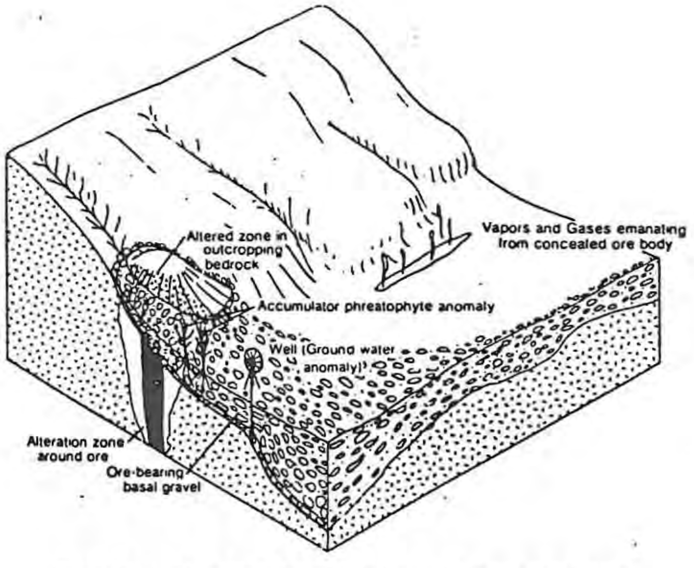
Sketch diagram of geochemical anomalies related to ore deposits that crop out at the surface or are concealed only by residual soil or colluvium — Type 1.



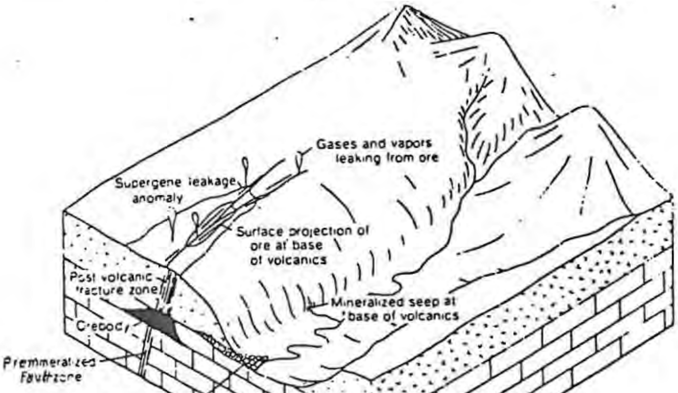
. Sketch diagram of geochemical anomalies related to blind ore deposits concealed beneath barren host rock — Type 2.



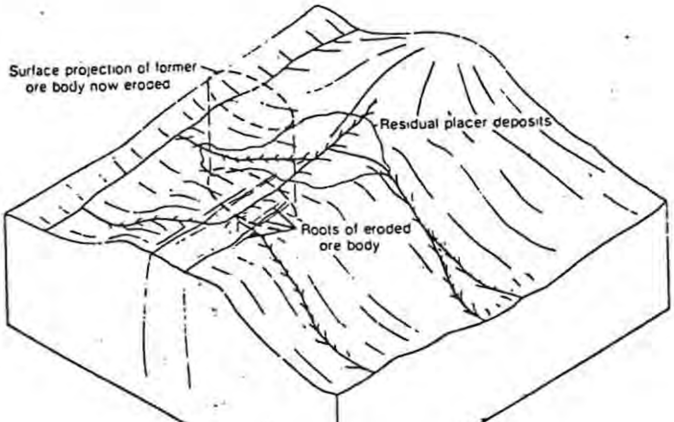
Sketch diagram of geochemical anomalies related to blind deposits concealed by pre-mineralization rocks — Type 3.



Sketch diagram of geochemical anomalies related to blind orebodies beneath permeable pediment fill — Type 4.



.. Sketch diagram of anomalies related to blind ore deposits covered by younger volcanic rocks — Type 5.



'. Sketch diagram of false anomalies related to ore deposits that have been removed by erosion.

Fig. 3.14B. Conceptual geochemical models related to concealment of ore targets. From Lovering and McCarthy (1978).

Mineral deposits are commonly concealed by relatively recent deposits of glacial debris, alluvium, colluvium, peat, windborne material, and volcanic debris, which effectively prevent any direct observation of mineral deposits that occur at the surface of the bedrock. The type and thickness of the transported overburden are the dominant factors effecting the development and nature of secondary geochemical halos. Mineral deposits covered by thick overburden are screened from the surficial processes of weathering and soil formation. Dispersion patterns are, however, developed in transported overburden by mechanical and hydromorphic processes.

The mechanical dispersion of particles derived from the erosion of mineral deposits results in syngenetic anomalies in the transported overburden. The mechanical movement of the solid particles by ice, water or wind, responsible for the transported overburden, forms dispersion halos in the direction of transport. The dispersion halos are best developed in the immediate vicinity of the source and decay rapidly with distance as a result of dilution by barren material. The syngenetic anomalies are comprised of fragments of mineralized rock, resistant ore minerals, and mobile elements locally dissolved and reprecipitated in the transported overburden. The anomalous material may be derived by direct physical erosion of the mineral deposit, by erosion of anomalous residual overburden, or by reworking of earlier anomalous transported overburden. Sygenetic anomalies derived directly from primary and residual geochemical halos, which are the best developed and most easily interpreted type, are only developed in the basal horizon of layered transported overburden (e.g. Fig. 3.15).

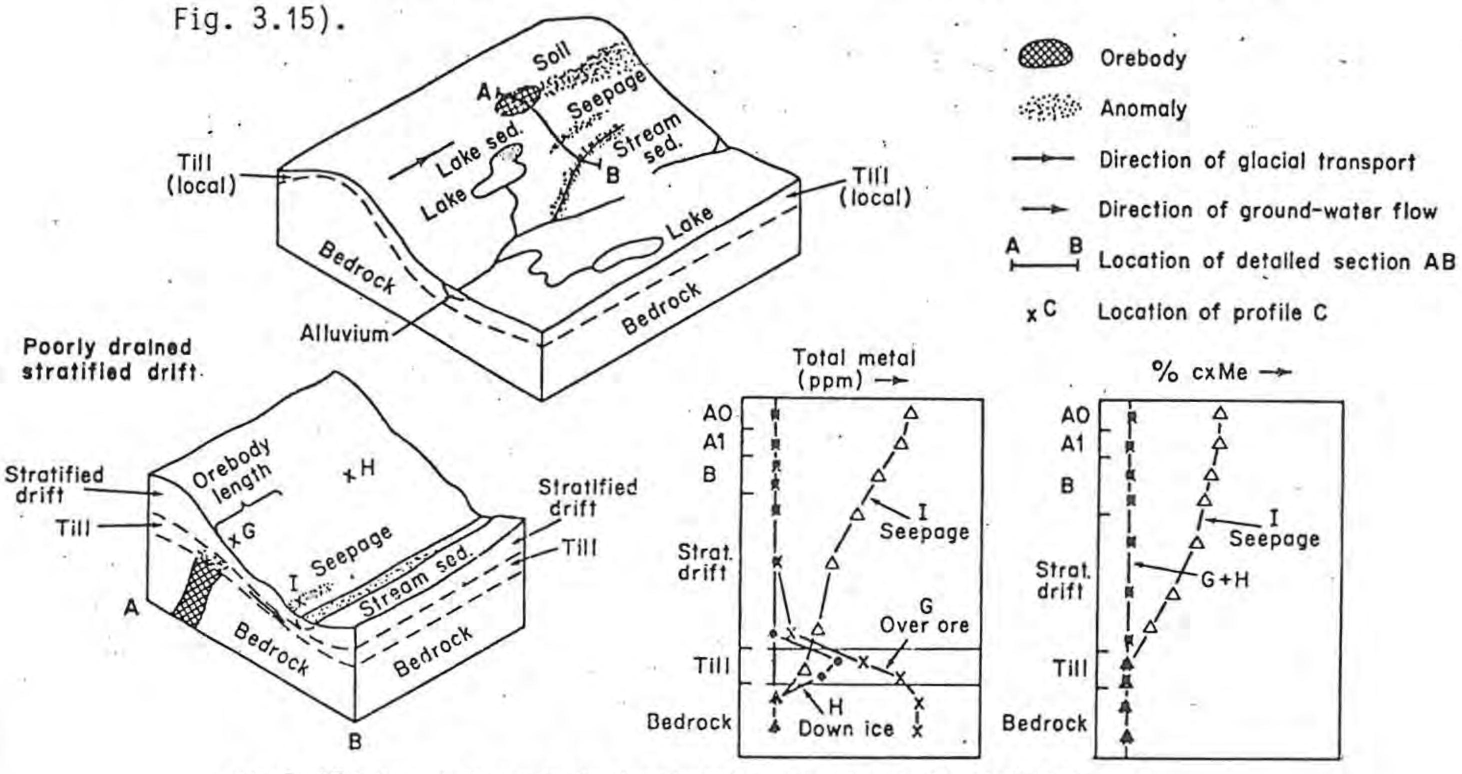


Fig. 3.15 Schematic diagrams showing dispersion of mobile metal in glacial overburden, and profiles of total and readily extractable metal in soil and glacial deposits. (After Bradshaw, 1975.)

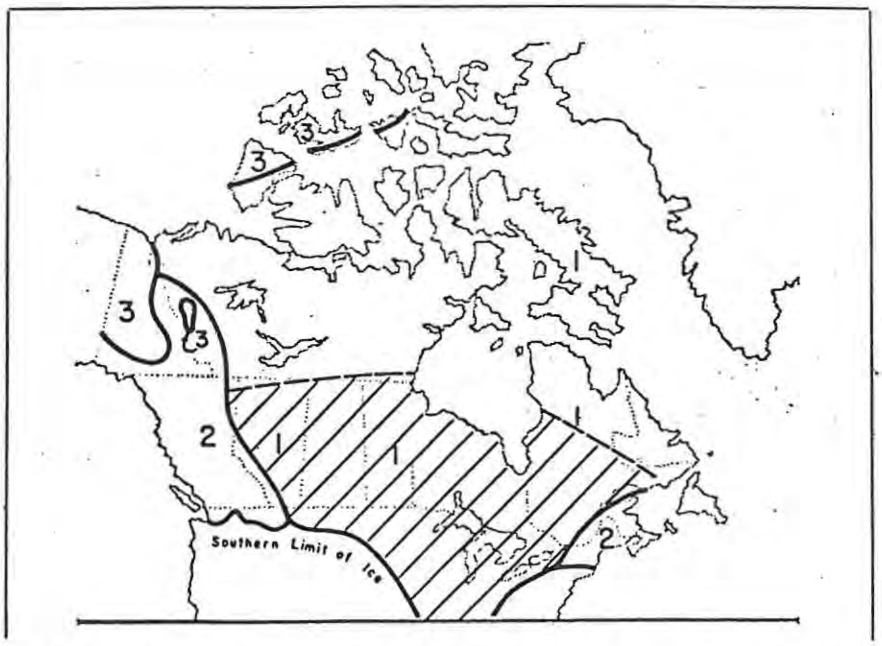


Fig. 3.16. Pleistocene glaciation in Canada and the approximate distribution of residual and non-residual soil (cross hatched) 1. Continental ice cover. 2. Valley glaciated areas. 3. Unglaciated areas. From Bradshaw et al (1972).

Modern soil profiles are commonly developed on transported overburden and resemble residual soils developed over weathered bedrock. Geochemical dispersion patterns in soils developed on thick transported overburden will reflect the geochemical patterns in the overburden and not the primary geochemical patterns.

Epigenetic anomalies are formed in transported overburden and soils where primary and secondary dispersion patterns below or in the transported overburden are subjected to hydromorphic and biologic dispersion. The mechanism of formation and the characteristics of the epigenetic anomalies are the same as those developed in residual overburden, although interpretation may be complicated by the derivation of epigenetic anomalies from transported sygenetic anomalies.

The interpretation of geochemical surveys in areas with transported overburden requires careful evaluation of the source of the overburden, the mode, direction and distance of transport of material, as well as the factors such as element mobility, climate and topography, soil types and profiles, etc., which must be considered in the interpretation of residual secondary geochemical anomalies. The factors affecting the interpretation of geochemical anomalies in transported overburden have been extensively investigated in the glaciated terrains of Canada and Scandinavia, Levinson (1974 Ch. 11), Bradshaw et al. 1972 and Kauranne (ed. 1976) and reference to these studies is recommended for an understanding of the basic principles involved in geochemical exploration in areas of transported overburden.

Bradshaw et al (1972) defined three areas in Canada, on the basis of glacial history, which have fundamentally destinct geochemical links between the primary and surficial environments (Fig. 3.16). The valley glaciated areas of the Canadian Cordillera are typified by transported overburden comprised of thin locally derived till. Sygenetic and epigenetic anomalies are developed in the till near most mineral deposits. The transported overburden shows similar geochemical characteristics to residual overburden with minor dislocation and smearing of mechanical anomalies and occasional blanketing of geochemical expression in areas of thicker overburden. The continentally glaciated areas of the Canadian Shield, on the other hand, are geochemically more complex due to a number of pleistocene glacial events resulting in variable mechanical dislocation of overburden and the presence of transported glacial overburden of remote origin. The deepest till horizons tend to have anomalies of local derivation similar to those in the Canadian Cordillera, but large areas are effected by the deposition of a number of till horizons or by stratified drift of glaciofluvial origin which tend to mask the primary geochemical patterns. (Fig. 3.15) The thickness of locally derived till has little effect on the secondary geochemical halos, but the thickness of overburden of remote origin is an important factor.

The distance of transport and the thickness of transported overburden such as colluvium, alluvium, and aeolion sand, are also the major factors affecting the development of syngenetic anomalies. The composition and permeability of transported overburden affects the development of hydromorphic anomalies. Till, colluvium and coarse sandy alluvium are generally permeable and epigenetic anomalies can be readily formed by ground water movement. Clay layers in transported overburden impede the movement of water and can effectively stop the development of epigenetic anomalies at the surface.

Dispersion in aeolian deposits has not been widely investigated, but in general aeolian sands tend to mask geochemical anomalies by dilution of local material with sand derived from relatively distant sources.

The arid environments in which aeolian sands are normally deposited, tend to retard the development of epigenetic anomalies due to deep water-tables. Weak hydromorphic anomalies related to evaporation of vadose water could be developed in aeolian sands.

3.2.3. The effects of climate on the characteristics of the surficial environment.

The climate of an area is a measure of the average and extreme conditions of temperature, moisture, wind, pressure and evaporation over a long period of time. The regional climate directly affects the amount and nature of ground and surface-water and the depth of the water-table in an area. The type and amount of vegetation, the nature and depth of weathering, and the characteristics of residual soil profiles are also largely dependent on the regional climatic conditions. Climate is, thus, an important factor affecting element mobility and secondary dispersion. The climate of a region, particularly the temperature and precipitation, can therefore be used to predict some of the expected characteristics of secondary dispersion halos. The generatizations based on prevailing climatic conditions are, however, only a broad indication of the expected surficial processes and dispersion patterns in a region. Local variations in climate, caused by factors such as altitude, relief and proximity to ocean currents, and the balance between the effects of climate and other environmental factors affecting secondary dispersion should be evaluated in order to interpret a particular geochemical survey. The major effects of changes in the regional climatic conditions on the broad characteristics of the surficial environment are illustrated in Fig. 3.17.

a) The effects of climate on weathering, soil profiles and residual anomalies.

The processes of weathering and soil formation and the resulting soil profiles and residual anomalies discussed in section 3.1.0. are largely based on the characteristics of the surficial environment in temperature regions. Temperate, humid climates favour active chemical weathering, leaching of mobile constituents and the formation of well drained podsolic soil profiles (Fig. 3.8). The open chemical system active in the surficial environment favours the development of well defined residual, hydromorphic and biological geochemical dispersion patterns in the vacinity of mineral deposits.

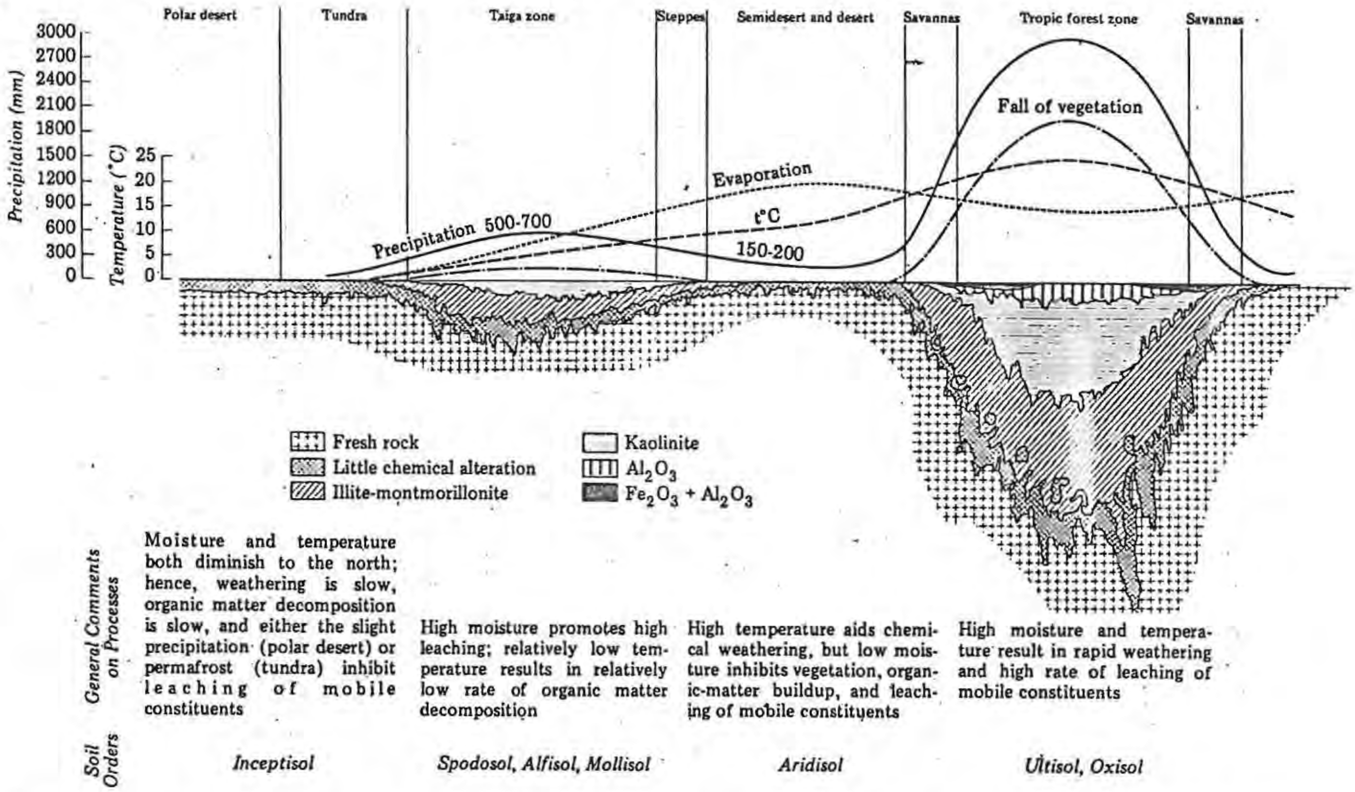


Fig. 3.17A. Diagram of relative depth of weathering and weathering products as they relate to some environmental factors in a transect from the equator into the north polar region.
From Birkeland (1974).

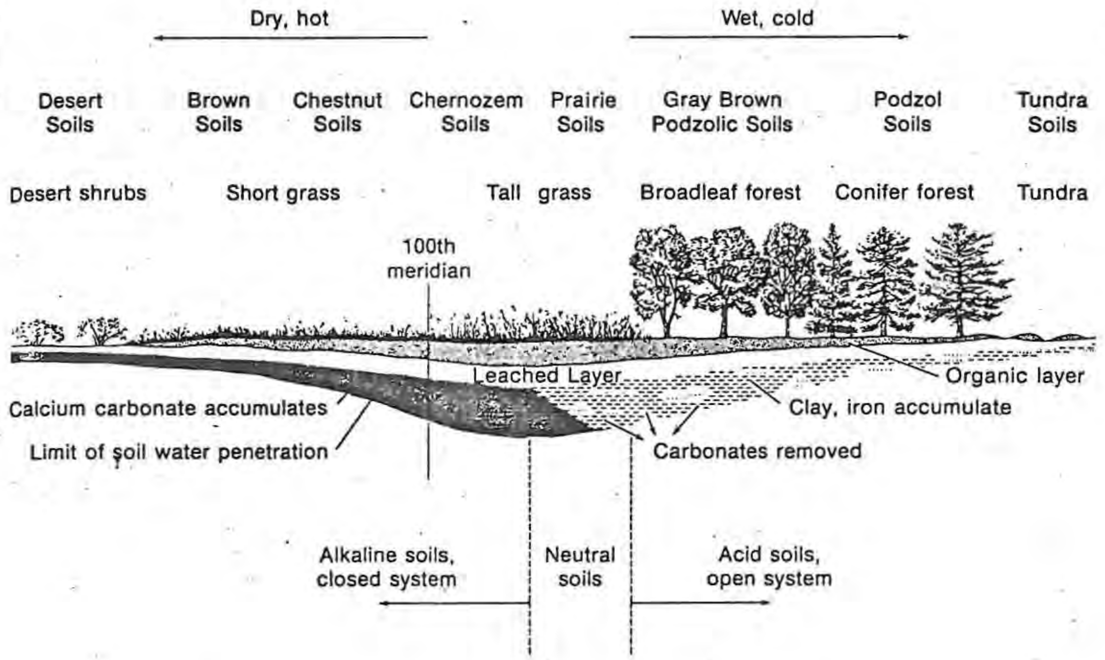


FIGURE 3.17B

Transect illustrating changes in soil profiles that accompany changes in vegetation and climate between the tundra in northern Canada and the deserts in southwestern United States. At the 100th meridian the annual precipitation averages about 20 inches; there and to the west the soils are alkaline. The easternmost grassland soils are about neutral; farther east the soils are acid.

From Hunt (1972).

Regions with hot, humid climates and abundant vegetation are characterized by rapid, deep weathering and extensive leaching of mobile constituents. The soil profiles are characteristically thick and freely drained. The upper horizons are acidic and extensively leached, due to abundant decomposing vegetation, and the B horizon is characterized by enrichment of Fe and Al. Residual dispersion halos are generally well developedin the B horizon of sub-tropical soils and can be successfully used for geochemical exploration, although the thickness of the leached horizon may cause practical problems. Hydromorphic dispersion is favoured by free movement of acidic ground water and epigenetic anomalies in the soils of seepage areas (e.g. in the dambos of Zambia described by Webb and Tooms, 1959 are good indicators of mineral deposits).

Prolonged weathering and leaching in tropical environments results in the development of lateritic soil profiles which are characterized by the accumulation of Fe- and Al-oxides and the removal of all other elements, including silica. No obvious relationships between soil chemistry and bedrock chemistry are retained in the lateritic profiles due to the gross redistribution of elements involved in their development. Mineral deposits in deeply weathered lateritic environments are thus only reflected by dispersion halos in the lower portions of the saprolite horizons. The effects of tropical soil profiles and laterites on geochemical exploration are described by Friggins (1979).

The very lowand erratic precipitation of desert and semi-desert regions has a significant effect on the characteristics of the surficial environment. Chemical weathering, although aided by high temperatures, tends to be limited by low moisture content, deep water tables and sparse vegetation. Physical weathering is dominant in very dry deserts where the surficial cover consists mainly of gravel, rubble and wind blown sand between large areas of bare rock outcrops. The soils of less arid regions are generally poorly developed and coarse grained with a large proportion of rock fragments and a low content of organic matter. The soil profiles form closed chemical systems as evaporation generally exceeds precipitation and water does not move downwards to the water -table. Mobile constituents are retained in the soils which are characterized by the accumulation of calcium carbonate and other slightly soluble salts. The limited leaching of arid soils (pedocals) results in a high proportion of primary and secondary ore minerals in residual dispersion halos which tend to be limited in extent, but have high contents of indicator elements. Hydromorphic anomalies are generally not developed due to limited movement of alkaline ground water, except for elements which are mobile in alkaline environments (e.g. uranium). The calcrete layers developed in arid and semi-arid environments only have limited effects on the development of residual dispersion patterns and do not impede geochemical surveys (Joyce, 1976, pp. 151). The clacrete normally contains coarse fragments of ore or gossan in the vicinity of mineral deposits and may be used as a consistent sampling horizon. Calcrete layers developed by later transport of calcium carbonate (valley calcrete) and those which are commonly developed on deeply weathered landsurfaces by changes to drier climatic conditions can mask primary geochemical patterns (Friggins, 1979, pp. 96).

The cold, wet (tundra) and cold, dry (polar desert) climates are characterized by a slow rate of weathering and slow decomposition of organic matter. Leaching is inhibited by low precipitation and by permafrost. Soil profiles are generally poorly developed and factors such as frost heaving and other cryogenic processes disrupt and destroy layering in the soil profiles. Impeded drainage due to glacial action and to permafrost conditions results in the extensive development of bogs and gley soils. The presence of transported overburden of glacial origin is an important feature of regions with cold climates. The use of geochemical exploration in regions of cold climate with a history of glacial action requires special considerations and many of the factors involved are discussed by Bradshaw (1975), Bradshaw et al. (1972) Levinson (1974) and Kauranne (1976).

b) The effects of climate on dispersion in drainage systems.

The balance between precipitation and evaporation in an area controls the amount of surface and ground water in the surficial environment. High rainfall areas, with precipitation in excess of evaporation, have relatively shallow water-tables, free movement of ground water and permanent surface drainage. Chemical weathering and acidic natural waters favour the formation of true and colloidal solutions, which increase element mobility, and hydromorphic dispersion trains associated with fine grained stream sediments are better developed than mechanical dispersion trains.

In regions of low, seasonal rainfall smaller drainages have only intermittent flow and hydromorphic dispersion is limited.

Mechanical dispersion of mineral grains, and rock and gossan fragments with the coarser grained stream sediments is characteristic of environments where evaporation exceeds precipitation. The dilution of the fine grained fraction of active stream sediments by aeolian sand is a further feature affecting the dispersion trains of desert environments. Huff (1971) and Lovering and McCarthy (1978) discuss the characteristics of dispersion trains in various drainage sediments in arid environments.

3.2.4. The effects of relief on the characteristics of the surficial environment.

The elevation of the land surface is a function of tectonic processes affecting the earth. The dynamic processes of the surficial environment act on uplifted lithosphere to reduce differences in elevation caused by tectonic activity. The balance between the accumulation of surficial material by weathering and soil formation, the removal of unconsolidated material by denudation, erosion and transport, and the accumulation of transported material by deposition is controlled by elevation and relief.

The effects of relief on the characteristics of the surficial environment and secondary dispersion patterns are generally gradational within an exploration area, but the general trends can be illustrated by considering areas of high, moderate and low relief seperately.

a) Areas of high relief.

Mountainous terranes often have pronounced changes of climate and vegetation related to changes in altitude between the peaks and the valley areas. Relief affects the rainfall patterns of an area. Micro climatic conditions and vegetation are also affected by the angle and direction of slopes. The climate and vegetation changes cause large variations in the balance between weathering and erosion. In general, the steep slopes and large differences of elevation in mountainous terranes favour physical weathering and mechanical dispersion of surficial material. The higher peaks, particularly those above the snow line, are characterized by bare rock faces, as debris tends to be removed by denudation at a faster rate than it can be formed by weathering. Chemical weathering, even in climatic conditions favouring vigorous chemical attack, tends to be concentrated on the decompostion of mechanically dispersed fragments. Mineral deposits and primary dispersion halos, thus, tend to be exposed at the surface and secondary dispersion halos are largely composed of primary and secondary ore minerals and mineralized rock fragments.

Mountain soils vary from poorly developed rocky soils in actively eroding areas to zonal soils in areas of accumulation. Relief and altitude combine to impart specific modifications to the zonal soil type most nearly characteristic of the local climatic conditions. Residual dispersion patterns in areas of high relief are complicated by a number of factors which make the interpretation of soil geochemical surveys difficult and reduce their value as an exploration technique. The factors include:

1) Active movement of material by soil creep and other denudational processes which distort and disrupt residual halos. Transported soils and colluvium are common and tend to cover geochemical patterns in areas of accumulation.

11) Truncated soil profiles, due to variations in the rates of erosion and denudation, caused by tectonic instability, further complicate the interpretation of geochemical patterns.

111) Leaching is dependent on the relative rates of weathering and erosion which are highly variable in mountainous terranes.

The drainage systems of mountainous terrane have steep gradients with active erosion in the catchment areas and rapid transport of sediments. Mechanical dispersion patterns are characteristically developed in the drainage systems. Hydromorphic patterns are only significant in tropical areas where element mobility is increased by rapid chemical weathering and a high content of organic compounds and humic substances in ground and surface-waters. The well developed drainage systems, active erosion and generally well defined mechanical dispersion patterns, as well as the fact that streams are the main access routes, make stream sediment sampling the best geochemical exploration method in areas of high relief. The loss of fine sediments in fast flowing streams can affect dispersion patterns in areas of rapid chemical weathering, but dispersion trains in coarse material are generally well defined. The use of the coarse stream sediment fraction for geochemical exploration is particularly favourable in mountains with cold and/or dry climates where physical weathering and mechanical dispersion are the most active surficial processes.

Large volumes of colluvial and alluvial overburden tend to accumulate in valleys or on alluvial fans where the drainage systems leave the mountains. The factors affecting geochemical exploration in areas of high relief with significant amounts of colluvial and alluvial overburden are illustrated by the models of the Basin and Range Province described by Lovering and McCarthy (1978). The effects of glaciation in mountainous terranes are illustrated by the geochemical landscape models of the Canadian Cordillera compiled by Bradshaw et al. (1972).

b) Areas of moderate relief.

The characteristics of the surficial environment and dispersion patterns discussed in section 3.1.0. are largely based on the ideal situation encountered in areas of moderate relief. The processes of weathering and soil formation of these areas are largely dependent on the climate and vegetation as there is generally a balance between the accumulation of weathering products and the removal of material by denudation and erosion. Residual geochemical patterns are well developed on the interfluves of drainage systems and are only locally transported by denudational processes on slopes. Local variations of soil types between upland and valley areas are developed, but the effect of different soil types on geochemical dispersion patterns is limited. Humid areas of moderate relief are characterized by free movement of ground water and the formation of hydromorphic dispersion patterns, particularly in well drained hilly country. The development of deep leaching profiles is favoured by moderate relief in tropical regions.

Hydromorphic dispersion patterns in fine grained drainage sediments are typical of the well developed drainage systems of humid regions with moderate relief. Deep water-tables and infrequent flow of streams limit hydromorphic dispersion in dry areas, but the dry streams can still be used for geochemical exploration if the characteristics of mechanical dispersion patterns in various size and compostional fractions of sediments are evaluated (Huff, 1971).

c) Areas of low relief.

Areas of low relief are characterized by the stagnation of the processes normally active in the surficial environment. Sluggish ground and surface-water movement slows down the mechanical and hydromorphic dispersion of weathering products. Shallow water-tables, particularly in river valleys, result in the formation of water logged gley soils in humid areas and saline soils in more arid areas. Accumulation of transported overburden in low lying areas tends to mask primary geochemical patterns.

Large regions of low relief are generally not favourable areas for geochemical exploration. They can be divided into the following broad categories which pose different problems for geochemical exploration.

1) Flood plains and internal drainage basins. Transported alluvial cover and waterlogged or saline soils are the major factors affecting geochemical exploration.

11) Uplifted areas of flat lying sedimentary or volcanic rocks (e.g. the Great Plains of North America) where the surficial geochemical patterns reflect only the upper sedimentary or volcanic units.

111) Continentally glaciated areas (described in section 3.2.2.).

1V) Erosion surfaces. The affects of erosion surfaces on geochemical exploration are discussed in section 3.2.5.

3.2.5. The effects of tectonic history and environmental changes on secondary dispersion patterns.

The interpretation of geochemical dispersion patterns in the surficial environment requires an evaluation of the evolution of the landscape through time. The major environmental factors affecting the processes active in the surficial environment undergo gradual changes with time and affect the evolution of the landscape. The characteristics of secondary dispersion patterns associated with a particular type of mineral deposit in Western Australia are, thus, different from those associated with a similar deposit in the Canadian Shield, in spite of similar primary dispersion patterns. The characteristics of secondary dispersion patterns can be predicted by evaluating the landscape evolution of the area in which the deposit occurs. The tectonic and climatic history of an area are the major variables which affect the characteristics of geochemical dispersion patterns in the surficial environment.

Tectonics control the level of exposure of primary geochemical patterns and the relief of an area. Tectonically active regions are characterized by high relief which favours erosion and denudation.

Surficial material is actively removed from higher areas and deposited as transported overburden in low lying areas. The energy of the environment is recharged by continued tectonic instability and the system remains dynamic. Tectonic stability, on the other hand, allows the processes of erosion and denudation to reduce the relief of the landscape. The balance of the surficial processes is shifted such that erosion and denudation of material are matched by accumulation of surficial material from weathering and soil formation. The environment reaches a state of dynamic equilibrium and drainage systems form regional base levels. Prolonged tectonic stability results in the denudation of the landforms, the development of erosion surfaces and the stagnation of the surficial processes.

Climate controls the rate at which the various processes of the surficial environment proceed and the affects of climate are superimposed on the erosion cycle described above. Climatic changes, which are indirectly related to tectonics by processes such as continental drift, uplift of land masses and orogeny, may complicate or destroy earlier geochemical dispersion patterns in the surficial environment.

The secondary geochemical patterns of tectonically active regions can generally be interpreted in terms of recent environment controls due to continual rejuvenation of the landscape. The Basic and Range Province described by Lovering and McCarthy (1978) serves as an example. The geochemical patterns of the area are largely related to physical weathering and mechanical dispersion in an arid environment caused by the rain shadow of the Seirra Nevadas. Freshwater lake-bed sediments, preserved in the alluvium of the basins, are evidence of an earlier humid climate, but rapid erosion due to tectonic instability has destroyed the influence of humid climatic conditions on the geochemical dispersion patterns of the ranges.

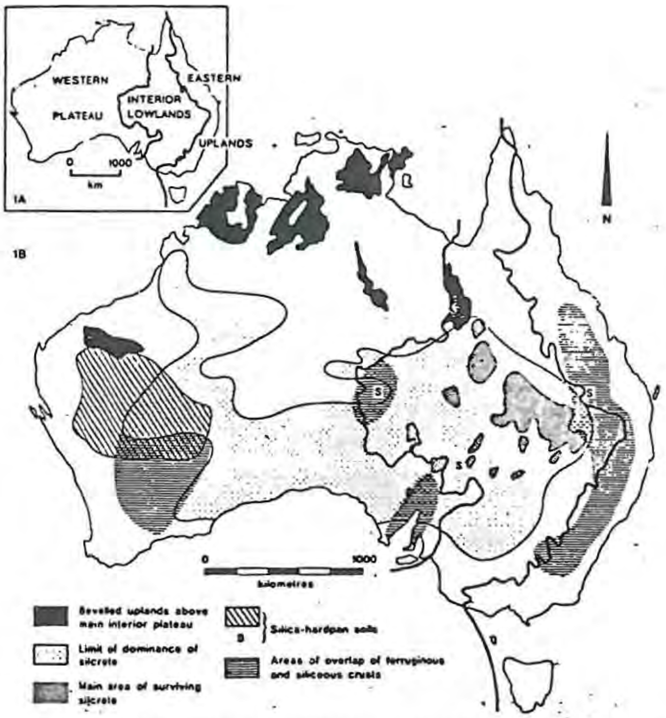
The secondary geochemical dispersion patterns related to present environment controls may be superimposed on the effects of earlier environments in tectonically stable areas. The resultant complexity of dispersion patterns is strikingly illustrated by leached deep weathering profiles associated with erosion surfaces in arid environment. The erosion surfaces, such as the land surfaces of Southern Africa discussed by Corbett (1978), are developed by the mature phases of the erosion cycle characterized by the stagnation of processes in the surficial environment. Deep weathering profiles commonly associated with the erosion surfaces are developed by highly active surficial processes during earlier phases of the erosion cycle. Mabbutt (in Butt and Smith, 1979) makes the following statement in connection with deep weathering profiles in areas of low relief in Australia:

> "Many deep profiles are, however, conformable with landforms of appreciable relief, and weathering may in fact be accentuated by topography as shown by deeper kaolinitic profiles at piedmont junctions and beneath valleys, due to heightened influent seepage and increased ground water flow. Deep kaolinitic weathering need not therefore imply base levelling, and certainly not a situation close to sea level."

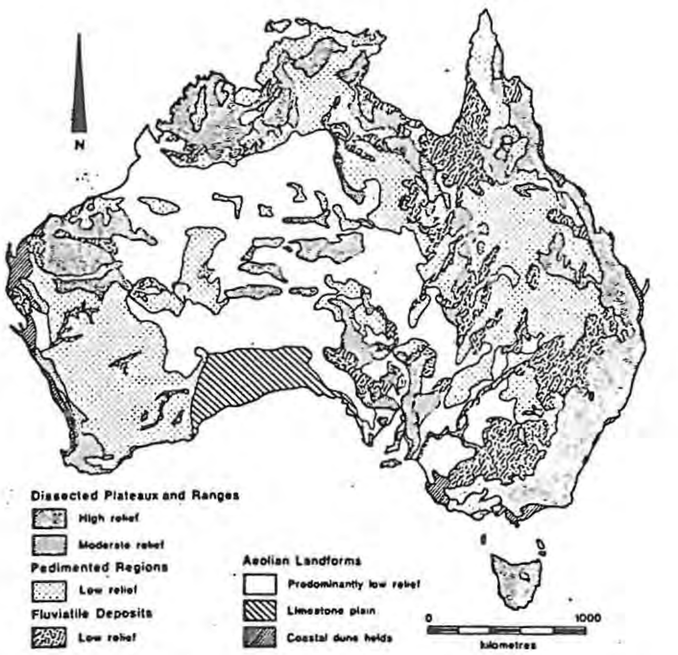
The geochemical patterns in regions of relative tectonic stability must, thus, be interpreted in terms of the geomorphological evolution of the region, and not only in terms of the present environmental conditions.

The interpretation of geomorphologically complex enviroments requires the establishment of a starting point from which the evolution of the geochemical landscape can be evaluated. The simplest example of a regional geochemical base level is the Quaternary glaciation of North America, Europe and Asia. The characteristics of secondary geochemical dispersion halos in the regions can be interpreted in terms of the glacial history and subsequent environment conditions as illustrated by Bradshaw et al (1972) and Kuaranne (1976). The geomorphological evolution of Australia and the characteristics of the associated geochemical dispersion patterns, described by Butt and Smith (1979), serves to illustrate the principles involved.

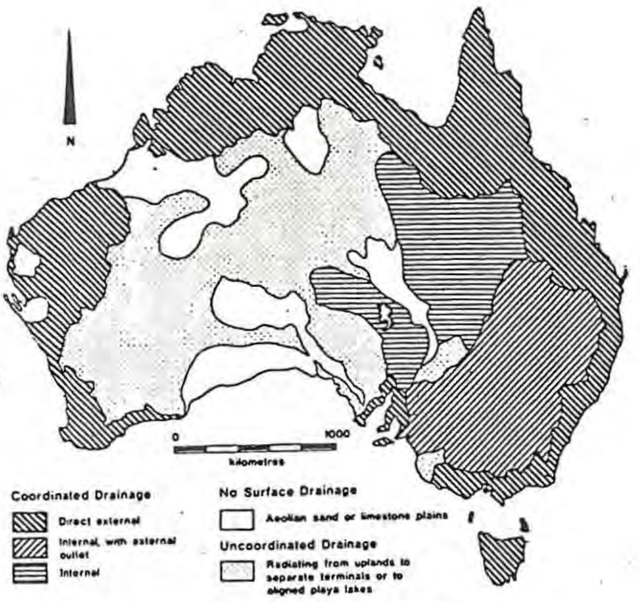
The landscape evolution in parts of Australia has resulted from 250 m.y. of subaerial exposure. Permian glaciation, similar to the Quaternary glaciation of the Northern Hemispher, gave a fresh start to the landscape evolution. The Western Plateau and interior Lowlands of Australia (Fig. 3.18) were tectonically quiescent, except for epeirogenic movement during the period from the Permian. The epeirogenic movements allowed marine sedimentation during late Mesozoic and Tertiary submergence, with subaerial weathering during the intervening periods of uplift. The Eastern Uplands, however, were tectonically active with significant Mesozoic-oligocene uplift.



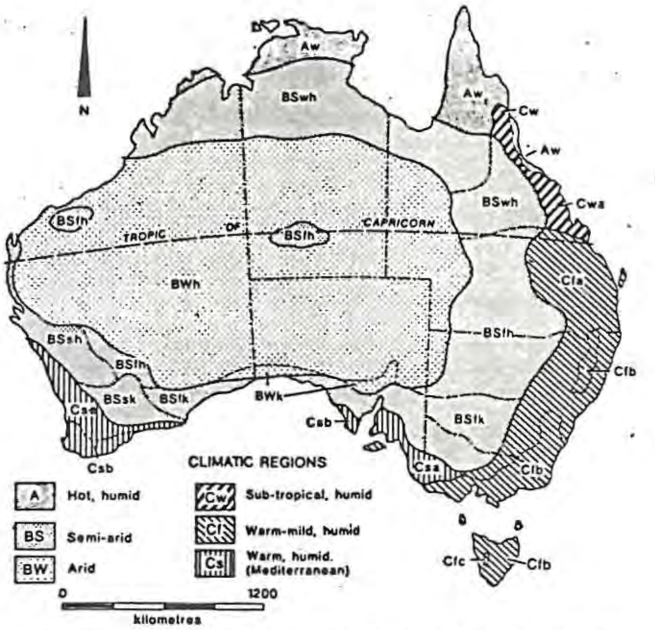
1. A. Main geomorphological sub-divisions of Australia. B. The distribution of silcretes and siliceous hardpans.



2. Relief and landform regions (modified after H.M. Churchward (unpublished) and Mabbutt, 1973).



3. Drainage divisions of Australia (after Mabbutt, 1973).



4. Climatic regions, using Köppen 1936 system modified after Gentilli, 1972.

Fig. 3.18. Regional environmental sub-divisions of Australia.
From Butt and Smith (1979).

Exposed bedrock was subjected to weathering under a range of climatic conditions during the period since the Permian glaciation. The Mesozoic climate was broadly temperate to warm, becoming humid tropical or subtropical in the Oligocene-Miocene. The more stable areas developed a mantle of deep lateritic weathering under the influence of the humid climates. The tectonically active areas were characterized by continued dissection during and after the major periods of deep weathering. A trend to aridity has characterized the climatic conditions since the Miocene. The arid conditions spread from the centre of the continent. The present climatic conditions reflect the trend to aridity (Fig 3.18) which was accompanied by extensive planation and partial erosion of the deep weathering profiles. The arid and semi-arid regimes resulted in declining competence of rivers, deposition in the river valleys, choking of the drainage systems and the development of playa-lakes and internal drainage. The present arid and semi-arid conditions of central Australia are characterized by the formation of calcrete, creek laterites and siliceous hardpans (Fig 3.18). The warmer and more humid climates of the peripheral regions are characterized by active weathering and erosion. Deep weathering profiles are still being developed in some areas and are being actively eroded in other areas (Fig. 3.19).

The combined affects of tectonism and climatic change in Australia have resulted in a wide range of landform situations characterized by different geochemical dispersion patterns which are largely controlled by the state of erosion of the deep weathering mantle (Fig. 3.20). The characteristic expression of mineralization in the surficial environment of various landform situations is illustrated by the conceptual geochemical models and case histories presented in Butt and Smith (1979). The Australian models, and the studies by Corbett (1978) and Friggins (1979) have significant implications for the understanding and interpretation of the geochemical landscape in southern Africa.

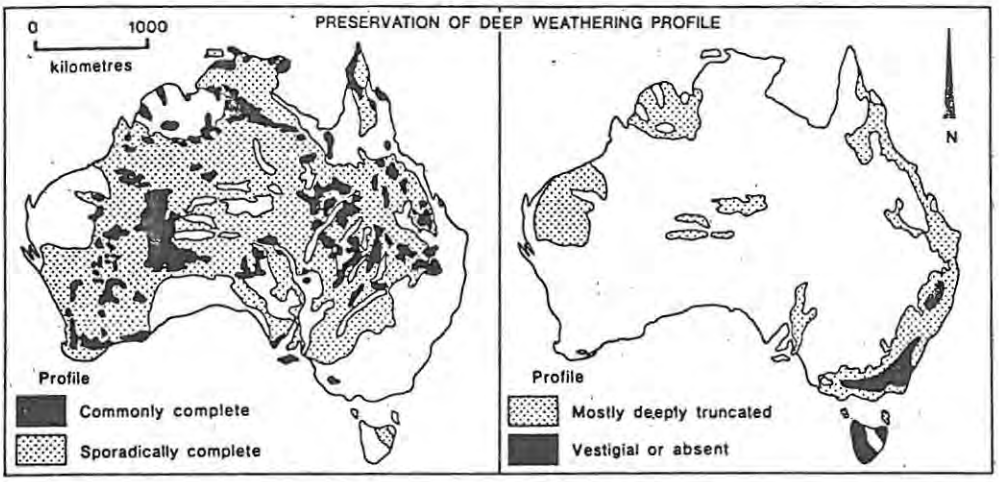


Fig. 3.19. Maps showing the preservation of deep weathering Profiles in Australia. From Butt and Smith (1979).

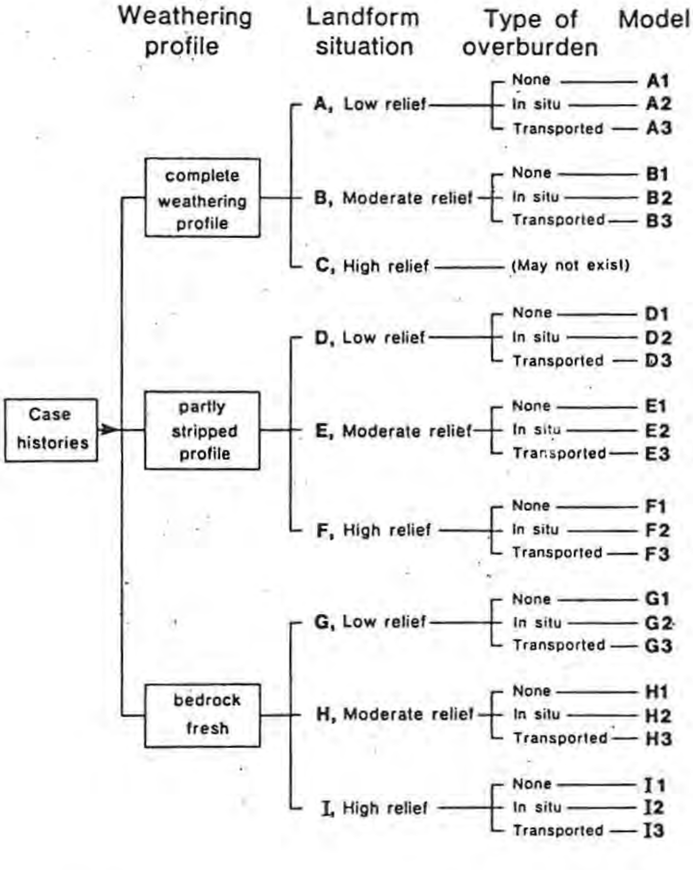


Fig. 3.20. The Hierarchical classification of landform situations and conceptual geochemical models in Australia. From Butt and Smith (1979).

4.0.0. SAMPLING FACTORS.

Berman's corollary to Robert's axiom:
"One man's error is another man's data". (Bloch, 1980)

4.1.0. The Design of Geochemical Exploration Programmes.

4.1.1. The basic concepts of sampling design.

Geochemical exploration techniques involve the measurement of one or more chemical properties of samples of naturally occurring material. The results obtained and their distribution are used to indicate the occurrence of a mineral deposit or favourable areas in which mineral deposits may occur. The procedure may be regarded as a chain of events having three links viz. sample collection, sample analysis, and interpretation of geochemical data. The entire exploration procedure is worthless if any of the links is incorrectly carried out. Sample collection is a critical phase in that the later steps in the procedure are largely based on the samples and information collected during the sampling programme. The importance of reliable sampling is further emphasized by the following facts:

a) Sample collection is the most expensive part of geochemical exploration projects.

b) Detection of unreliable samples at a later stage in the exploration procedure is difficult.

c) The resampling of an area is just as expensive as the initial sampling as labour and transport are the major cost factors.

The interpretation of geochemical data involves both geological and statistical inference, and successful interpretation is, thus, largely dependent on the design of the sampling programme. The sampling design should be done with particular interpretation methods in mind and should be sufficiently flexible to permit a progressive sequence of increasingly complex interpretative attempts. The objectives and budget of the overall exploration programme, the characteristics of the deposits sought, the geological and geomorphological factors that influence geochemical dispersion patterns, and the statistical requirements of samples have to be considered in making decisions on the following basic concepts of sample collection:

a) The type of material to be collected during the sampling programme. (What?)

b) The geological and geomorphological locations from which the material should be collected and the relative spatial distribution of sample locations. (Where?)

c) At what stage during the exploration programme a particular type of sample should be collected. (When?)

d) The sampling method to be used. (How?)

e) The qualifications required of the sampler. (Who?)

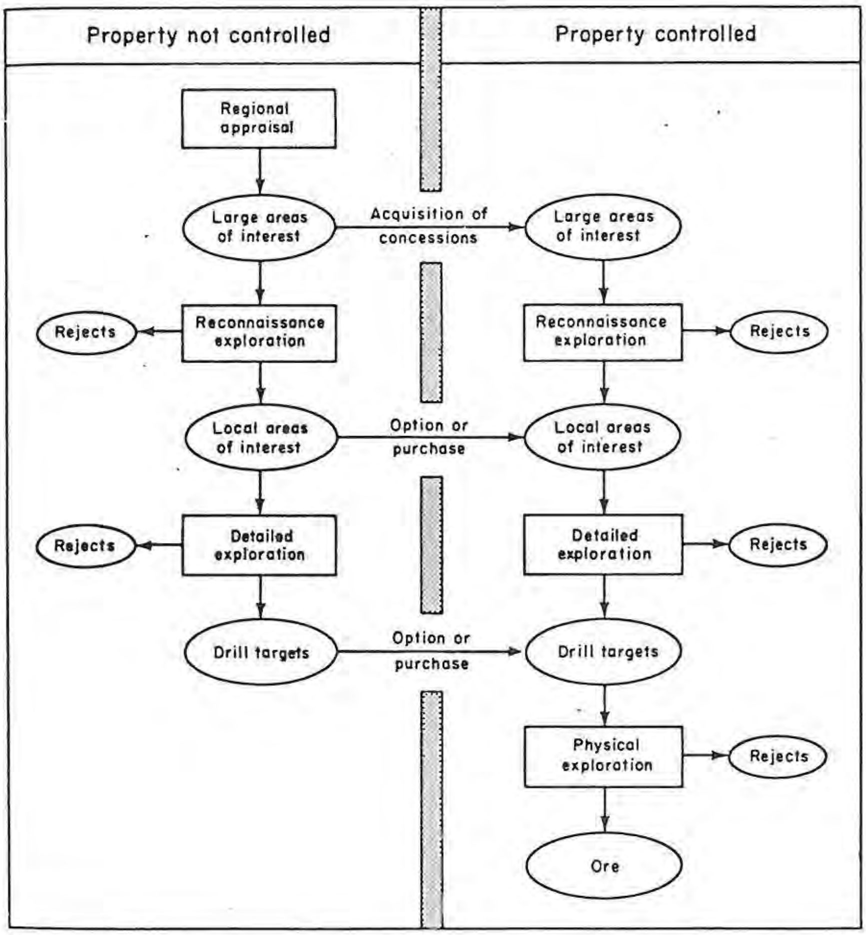


Fig. 4.1. Sequence of operations in an exploration programme. From Rose, Hawkes and Webb (1979).

The design of geochemical exploration programmes will depend mainly on the objectives of the overall exploration effort and will essentially involve reconnaissance exploration surveys, detailed surveys and physical surveys (Fig. 4.1). Geochemical surveys, irrespective of the type of survey, must be deliberately planned as "an important aspect of exploration is the matching of a particular method to the objectives of a survey and the environment in which the survey will be conducted" (Levinson, 1980). The fundamental factors which should be considered in planning a geochemical survey have been enumerated by Joyce (1976, pp 115 - 124) and summarized by Levinson (1980, pp 787 - 790). The topics are listed in Table 4.1, but the reader is referred to the original texts for details.

Table 4.1. Factors that should be considered during the planning of Geochemical Surveys.

1. Decision on the type of ore deposit sought.
    a) Primary ore mineral(s).
    b) Associated minerals and elements.
    c) Probable localizing structures or rock types.
    d) Predicted grade and size of the deposit.
2. Decision on what type of dispersion pattern to utilize. (Refer to Sections 2.0.0. and 3.0.0.)
3. Choice of the element or elements to be analysed. (Refer to Section 5.3.1.)
4. Choice of sample material and method of collection. (Refer to section 4.2.0.)
5. Choice of suitable sample spacing.
6. Choice of an appropriate analytical technique. (Refer to section 5.0.0.)
7. Integration of theoretical and practical considerations.
8. Choice of data to be recorded.
9. Choice of interpretation methods. (Refer to Section 6.0.0.)
10. Recommendations on follow-up studies to assess anomalies.

The use of statistical inference during the interpretation of geochemical surveys places further constraints on the sampling design. Joyce (1974) summarizes the statistical requirements involved as follows:

"a) Variance of the results to be processed.

The total variance of geochemical data may be regarded as being composed of analytical variance, field sampling variance, lithological variance, mineralization variance and variance caused by secondary effects such as weathering. Suitable sampling and analytical methods must be chosen such that variance due to the other four causes does not mask the variance caused by mineralization.

b) Sample spacing.

Assumptions concerning the size, shape and orientation of a sought anomaly allow predictions to be made on the probability of collecting one or more samples from the anomaly using a specified sampling grid. There is a very low probability of intercepting some prospected targets using sample spacings which are economically feasible. Conversely, many subjective sampling designs are extravagant without appreciably increasing the probability of success.

c) Recognition of an anomaly.

Even assuming that the diverse variance components have been adequately dealt with in designing the programme and that a sampling pattern has been devised to intercept any anomalies present, there remains the problem of whether the anomaly will be recognized. The classical situation of data drawn from a single population upon which is superimposed a large addition of some element in a few samples because of mineralization is rarely encountered. Data are generally drawn from a number of overlapping populations. Thus a sample which is anomalous in one population may be concealed within an overlapping population. This is critical where anomalies are subdued (e.g. in stream sediments or in strongly leached soils). Therefore, at the design stage a decision must be made on whether single element data and relatively simple interpretation have the potential to recognize any anomaly or whether multi-element data and more complex statistical procedures must be used to ensure recognition of anomalous samples."

Objective decisions on sampling design can only be made if the type of mineral deposit sought and the characteristics of the primary and secondary geochemical halos associated with deposits of that type, in the geological and geomorphological environment of the exploration area, are clearly defined. The information required for the design of geochemical surveys must be obtained from orientation surveys. Published information on sampling programmes for similar mineral deposits in similar environments should be used to form a basic framework for the orientation survey. Subjective decisions on the concepts of sampling design, based on the experience (or lack of experience) of the explorationist, are probably the major reason why many geochemical surveys are difficult to interpret and unsuccessful.

4.1.2. Orientation surveys.

Geochemical exploration should be carried out in a series of logical steps in which each phase is more detailed than the last and serves to locate mineralization more closely. A multi-media orientation survey, preferably in the vicinity of known mineralization, should be done before the full scale geochemical exploration programme is initiated. More specific orientation studies should be conducted before each phase of a sequential exploration programme (e.g. an orientation study of the geochemical charateristics of dispersion patterns in soils before soil geochemical follow-up surveys in areas indicated as anomalous by regional stream sediment sampling).

The objective of an orientation survey is to determine the most economic means of gaining the best results from a geochemical survey. The orientation work should also establish if geochemical exploration is feasible in the exploration area. It is an essential part of any geochemical exploration programme because any area in which exploration geochemistry is done, is likely to be different (geochemically) from previously explored and studied areas. Orientation surveys are advocated by experienced geochemists, even in environments which appear to be relatively uncomplicated.

Orientation surveys include any form of studying the geochemical characteristics of an area before the routine sampling of the geochemical project is initiated. The studies are done in order to provide objective answers to the various aspects of sampling design discussed in the previous section and listed in Table 4.1. The nature of an orientation survey depends on the exploration situation (e.g. Plant, 1971). A standard format cannot be adopted as an orientation survey is essentially a scientific experiment to establish and quantify factors which will influence the full-scale geochemical survey. Bradshaw (pp 201-205, 1975) does however, recommend minimum standard requirements for multi-media orientation surveys. A comprehensive orientation survey is time consuming and expensive, but the operation can be considerably streamlined by a sound knowledge of the principals of geochemical exploration and the mechanisms of geochemical dispersion. Geological common sense and judgement should be applied in all instances to simplify the matter. Many case histories published in the literature are essentially orientation studies and should be used as a reference for the design of orientation surveys (but cannot replace them).

The aspects of orientation surveys which have important effects on the interpretation of geochemical surveys are:

a) The division of the exploration area into sub-areas which have comparable geochemical characteristics for the purposes of interpretation of analytical results. The division is done on the basis of lithology, pedology, topography, climate, type of surficial cover (transported or residual), soil types, drainage characteristics and other geological and geomorphological factors affecting the interpretation of geochemical surveys.

b) Selection of a sampling medium, sampling design and analytical procedure for each sub-area which will make interpretation as direct and as simple as possible by maximizing the contrast between background and anomalous analytical results.

c) Establishing the geochemical signature of the type (or types) of mineral deposit sought in each of the sub-areas.

d) Establishing the background characteristics of the various sub-areas.

e) Recognition of features which may cause false geochemical anomalies and determining their characteristic geochemical signatures.

The attitude that should be adopted during orientation work is summarized by the statement made by Levinson (1974) viz: "The time to ponder all the variables, and to test them out, is before the actual geochemical exploration begins, not after the samples have been collected".

4.1.3. Control and reliability of field work.

The interpretation of geochemical surveys is fundamentally a geological, rather than a chemical problem, and the important aspects of orientation, planning and sample collection should be controlled by an experienced exploration geologist or geochemist. The surveys usually involve the collection of a standard sample or set of samples from a large number of localities in the exploration area and reliable routine sampling must meet the following requirements:

a) The samples must be collected at the correct geographic locations and from the correct geological or geomorphological situation at each sample location.

b) The sampling of the correct material at each location such that all the samples collected are comparable. Sample collectors have to be able to recognize changes in geological or environmental conditions which may require the modification of the sampling techniques in order to get representative and comparable samples.

c) The correct handling of the samples in order to avoid contamination.

d) Correct numbering of samples and plotting of sample locations on maps or photographs in order to avoid confusion when the results are interpreted. The accuracy with which sample sites have to be plotted is largely dependent on the scale and objectives of the survey. The inaccurate plotting of sample positions can seriously hamper interpretation, but the efficiency of the survey can be affected by overly precise surveying of sample positions. Precise surveying of sample positions is generally only necessary during detailed follow-up surveys of in situ anomalies.

e) The recording of adequate geological, geomorphological and geographic information about the sample site. The data recorded can include anything which may be of value during interpretation of the survey and the information recorded is largely dependent on the nature and requirements of individual surveys. The information often requires subjective estimation of certain features and training of personnel is essential for comparable estimations. Standardized data sheets are required for computer based interpretation techniques and can also serve as a reminder of the factors which are important for each type of survey.

Maximum efficiency of geochemical surveys requires the use of trained teams of lower-grade personnel and local labour for routine sampling where possible. The requirements of reliable sampling and adequate recording of information have to be considered in evaluating the merit of using non-professional or professional personnel to do routine sampling. The use of professional personnel for routine sampling is generally advisable for reconnaissance type surveys during which a large amount of information relating to the geology, geomorphology and geography of the area must be collected. The combination of sampling and reconnaissance mapping is advisable in these situations. Trained non-professional field assistants can be used to do routine sampling in high density detailed surveys where the geological and environmental conditions are adequately understood. Strict control of all sampling operations by the geologist responsible for the interpretation of the survey is essential as confidence in the reliability of data is a major factor in the interpretation of geochemical surveys.

4.2.0. The Characteristics, Advantages and Collection of some Common Sampling Mediums.

4.2.1. The characteristics of a good sample medium.

The materials commonly collected during geochemical surveys are only indirect indicators of mineral deposits. The interpretation of geochemical data is, thus, largely dependent on the characteristics of the sample medium and requires basic assumptions to be made about the chain of events which accumulate the indicator elements in the material sampled. Factors such as the origin, transport and deposition of the sample medium affect the inferences that can be made on the basis of analysis of the samples.

The important characteristics that have to be considered when selecting material to be sampled are:

a) The material must be a reliable indicator of the bedrock geochemistry and especially of mineralization in the area.

b) The material should yield a wide primary or secondary dispersion halo, or a long dispersion train, of anomalous ore-related elements or compounds. The anomalous element in the halo or dispersion train should increase (or decrease) in a uniform and predictable fashion towards the ore target.

c) Material that accumulates and concentrates ore elements and other elements uniquely associated with ore deposits, but does not selectively concentrate elements from unmineralized rocks so as to cause false anomalies, should be favoured.

d) The material should be capable of revealing ore deposits concealed under a considerable depth of overburden or barren rock.

e) The material must be abundantly available in the area and must occur in such a way that comparable samples can be taken from a sufficient number of locations within the exploration area. The ease and speed with which the material can be collected and analysed should also be considered. Trout livers may be a good sampling medium (Warren et al, 1971), but their use in exploration projects would probably not be encouraged by budget minded exploration managers.

The characteristics of the sample material selected for a survey will put important constraints on the other variables involved in sample design viz. where, when, how and by whom. The constraints of the more common types of sample media and their effects on the interpretation of surveys is discussed in the following sections.

4.2.2. Stream sediment sampling:

Geochemical dispersion trains in drainage systems are normally best detected by sampling some form of active stream sediment (Table 4.2). The advantages of sampling any of the various sediment fractions are largely dependent on the geological and geomorphological factors affecting the dispersion patterns in the area being investigated. The advantages and disadvantages of stream sediment samples in various environments are discussed by Lovering and McCarthy (1978), Plant (1971), Davy, Rossiter and Wall (in Butt and Smith, 1979) and Huff (1971).

Stream sediment sampling is a reconnaissance exploration method capable of rapidly evaluating a large exploration area. The features reflected by stream sediment surveys and the detail of information which may be extracted varies considerably with the sample density employed and the size of the stream sampled. The optimum density depends on the mineral potential of a region, the type of deposit sought (e.h. porphyry copper deposits are reflected by fairly low density sampling), the nature of the drainage system, the reliability and extent of geological and geomorphological knowledge and the objective of the survey. A broad classification of the various types of stream sediment surveys and their advantages is given in Table 4.3.

a) Reconnaissance stream sediment surveys.

Reconnaissance sediment surveys are aimed at locating regional patterns which indicate areas of increased economic potential. The use

Table 4.2. Types of Stream Sediment Samples.

A. Active Stream Sediments.

1. Mixed sediment samples.

A sample of all the active sediment fractions gives a representative composite of all the material occuring in the catchment area; most favourable for low density reconnaissance sampling; collecting comparable samples from different sample locations is a problem; representative sampling may require the collection of a large composite sample with material being taken from a number of positions in the stream at each sample site.

2. Silt and clay sized sediments.

The fine fraction of the active stream sediments is the most commonly used sampling medium (normally the - 80 mesh fraction is sampled); favourable for detecting hydromorphic sediment anomalies; mechanically dispersed gossan fragments and most primary and secondary ore minerals are easily abraded during transport (particularly in arid areas) adding to the advantages of sampling clay and silt sized material; dilution by wind-blown dust is a problem in arid areas; downstream dilution and winnowing makes the sampling of low order streams more favourable; clay, Fe- and Mn-oxides and organic matter with adsorbed elements can be a problem in certain environments; advantages of various fine mesh sizes should be tested before the sampling programme; sieving should be done in the field to assure sufficient sample.

3. Sand sized sediment.

Sand sized sediments can be used if resistant ore minerals are expected (e.g. chromite, cassiterite, etc.) and in arid areas where dust dilutes fine sediments; the dispersion trains are generally shorter than fine sediment trains.

4. Coarse material.

Sampling of pebbles and cobbles has special application in areas of physical weathering and mechanical dispersion by streams with steep gradients and in areas of dominantly carbonate bedrock; mineralized and hydrothermally altered fragments are selected to indicate the type of mineralization in the catchment (Huff, 1971);
jasperiod fragments can be sampled (Lovering, 1981); chemically precipitated coatings on pebbles can be analysed (Chao and Theobald, 1976).

5. Heavy mineral concentrates.

Most ore minerals tend to concentrate in the heavy mineral fraction; dilution by lighter, barren rock-forming minerals (e.g. quartz, feldspar, mica) can be reduced by panning; care should be taken not to overclean the concentrate and lose the lighter ore minerals (e.g. limonite, chalcopyrite, malachite, etc.). Magnetite tails may have advantages in deeply leached environments e.g. dispersion trains from Gamsberg (McLaurin, 1978).

B. Bank Samples.

1. Active sediments deposited by major floods may be collected if a stream has been recently contaminated.

2. Seepage samples.

Seepage material (e.g. Fe rich ooze) can be sampled for hydromorphic anomalies as seepage areas are important precipitation barriers; samples are collected during routine stream sediment sampling
(e.g. Robiera, et al, 1979).

3. Break - in - slope soils.

Hydromorphic anomalies in break-in-slope soils can indicate the side from which anomalous material is entering the stream; used to follow-up stream sediment anomalies; may be collected during stream sediment surveys but only analysed when required to interpret doubtful stream anomalies as the break-in-slope soils reflect local conditions.

Table 4.3. CLASSIFICATION OF STREAM SEDIMENT SURVEYS (adapted from Bradshaw, 1972).

Size of area represented by each sample.	Size of Drainage sampled.	Objective of the Survey.
A. 100km² to 200km²	50km² depending on complexity of the geology	The recognition of geochemical provinces in large unexplored areas. (e.g. Sierra Leone Survey of Nichol, et al, 1966).
B. 10km² to 50km²	2km² to 25km²	The recognition of mineralized belts and similar broad geochemical features. (Methods A and B are generally most useful in areas of high rainfall where geology is difficult to map).
C. 1km² to 5km²	1km² 1st order drainages may be used if geology is not highly variable.	Indication of lithological types, rough location of geological contacts, more accurate location of mineralized belts, may indicate individual deposits (e.g. the survey of Northern Ierland, Applied Geochemistry Research Group, Imperial College, London, and the survey of part of the Namaqua Mobile Belt, South African Department of Mines, Geological Survey).
D. Detailed drainage surveys with close spaced samples along larger drainages and sampling of all small tributaries. Each sample represents the area upstream of the sample site.	The size of expected dispersion train controls the interval at which samples are taken along drainages. 1st order drainages are important.	The location of dispersion trains related to mineral deposits in economically favourable areas.

of the surveys is based on the assumption that the sediment sample collected gives a natural composite which is representative of the catchment area drained by the stream from which the sample is taken. The basic requirements for this assumption to be valid are:

1) The terrane must be uniformly dissected such that all the lithological units in the catchment area are represented by the sediment sample.

11) Streams must be actively eroding material derived from the bedrock in the catchment area.

The samples collected from a drainage system of a particular size must be representative of the larger area between sampled catchments. The uniformity of the geology will dictate the size of the area over which individual analytical results can be extrapolated. It is generally advisable to take samples from streams with small catchment areas and extrapolate the results over the larger area ascribed to the samples. Regions of complex geology may require the use of samples from streams with large catchment areas in order to obtain a representative sample. Samples representing larger catchment areas, however, tend to have lower contrast.

b) Detailed stream sediment sampling.

Detailed stream sediment sampling is aimed at locating secondary dispersion trains associated with individual mineral deposits. The surveys are detailed in terms of drainage sampling, but are still a reconnaissance exploration method. Samples are collected at intervals along the lower order stream channels and at locations directly above the junctions of streams. The sample spacing in the larger streams depends on the expected length of dispersion trains. Detailed stream sediment surveys should sample material giving the longest dispersion train with the highest intensity and contrast, based on information from orientation surveys. The sampling of more than one type of stream sediment is often advisable (even if only one fraction is analysed initially).

The reliability and interpretation of stream sediment samples is dependent on careful sampling and on detailed and comprehensive notes about the characteristics of the sample site and the catchment area. Some important factors which should be considered during stream sediment sampling are:

1) The presence of Fe- and Mn-hydrous oxides and organic matter in the sample which can concentrate indicator elements from background lithologies.

11) Geological contacts can cause abuild up of elements in stream sediments by changing the physical and chemical conditions in the streams (e.g. limestone can change the pH of stream water).

111) Dilution of stream sediments by bank material.

1V) Accumulation of indicator elements precipitated by mixing of stream waters of different composition.

V) Contamination of streams by human activity.

4.2.3. Soil sampling.

The sampling of residual soil is a cost effective method of exploring areas of unsatisfactory outcrop as the soils reflect the bedrock chemistry. Soils developed on transported overburden must, however, be distinguished before or during a survey as they will not reflect the bedrock chemistry. The sampling of soils developed on transported overburden is viable under certain conditions (see section 3.2.2.).

Important factors to be considered during soil sampling are:

1) Samples must be taken from a consistent soil horizon.

11) A grain size fraction which enhances the distinction between background and anomalous concentrations must be sampled (the -80 mesh fraction is commonly used, but is not necessarily the best fraction in all areas).

111) The use of a small mesh interval minimizes errors due to different element concentrations in the various size fractions of the soil.

1V) The clay, Fe- and Mn-oxide and organic content of soils has important effects on trace element distribution. Major changes in the constituents can usually be seen and should be noted during sampling.

The optimum soil horizon and size fraction should be selected by studying the trace element distribution in various soil types during an orientation study. The characteristics of the soil profile are best studied by digging pits or trenches. Changes in the characteristics of the soils noted during sampling should be investigated by further pitting as the cost of the extra work is justified by the increased confidence in the sampling results and by the added information available for interpretation. (When in doubt, dig a pit!!!)

a) Regional soil sampling.

Regional soil traverses (e.g. 500m line spacing x 50m sample spacing) are commonly used in flat areas where detailed drainage surveys can not be done. The problems associated with sampling of deeply leached land surfaces should, however, always be borne in mind in areas of low relief (section 3.2.5.). The distribution of soil types and broad lithological units should be mapped during the sampling program in order to simplify interpretation. Vegetation can often be used as a guide to the mapping of soil types and lithology in areas of deep residual soil. Sampling should be done across the regional strike and the probable size of dispersion halos should be considered in selecting traverse and sample spacing. Grids should be designed such that the line spacing is not greater than one third of the expected economic strike length and at least two samples on each line should fall within the expected width of an anomaly. Chain (or pace) and compass traverses are sufficiently accurate, but sample sites should be marked at intervals (e.g. 500m) so that anomalous sites can be accurately recovered at a later stage.

Soil samples can be collected along ridges and spurs in areas of moderate to high relief in order to close-off anomalies in stream sediment samples. Sample traverses carried out along the break-in-slope of drainage courses can be used to locate transported and hydromorphic anomalies in areas of moderate to high relief.

Isolated soil sampling traverses (with closely spaced sampling points e.g. 500m) along roads can be used as a reconnaissance method to indicate economically favourable zones in poorly drained regions. Experience in the Northwestern Cape has indicated that the method can be successful in semi-arid regions where the C soil horizon can be easily sampled (A and B horizons are poorly developed). Interpretation must however, be based on a subdivision of the sample populations according to lithological units mapped on a regional scale. Geomorphological and physiographic subdivisions of the area are also required (e.g. in the

Northwestern Cape samples from the Bushmanland Surface cannot be compared with samples from the Namaqualand area or from the Orange River valley).

b) Detailed soil sampling grids.

Detailed soil sampling grids are commonly used to follow-up reconnaissance geochemical and geophysical anomalies and to determine the possible extent of mineralization indicated by isolated mineralized outcrops. The grid spacing depends on the size of the follow-up area and on the expected size of the potential mineral deposit. A series of sampling grids with tighter sample spacings may be used to reduce the target area until the size, shape and axis of the potentially mineralized target have been defined. A number of soil pits should be dug on anomalies as they can help to define the exact location of the anomaly source, particulary if the anomaly peak is displaced by the effects of denudational processes on the residual soils. Detailed soil sampling grids should be accurately surveyed and disigned to suite the interpretation method.

Soil samples are collected using a variety of tools depending on the depth and nature of overburden. The best method should be defined by orientation work and is often a matter of personal preference. Samples must, however, be taken from a consistent soil horizon and methods which rely on sampling from a consistent depth (e.g. using a mattock) should be avoided as the thickness of soil horizons varies. The amount of sample material that should be collected depends on the dispersion of the anomalous constituents in the soil (e.g. C horizon sampling where resistant minerals are inhomogeneously distributed will require a larger sample than B horizon sampling where secondary and hydromorphic constituents are evenly dispersed). A 20 to 50 gram sample will normally provide enough material, but the sample size should be defined by orientation work for reliable results and successful interpretation.

4.2.4. Rock Sampling.

The sampling of fresh and weathered bedrock is an important part of all mineral exploration programmes. The major objectives of bedrock sampling, which dictate the type of bedrock material sampled and the sampling design, are:

1) to establish the presence of the ore elements in the exploration area.

ii) to provide essential information on the background abundances of elements analysed in soil and sediment surveys.

iii) to detect distribution patterns of elements that are spatially related to mineralization.

The common types of bedrock material that can be sampled, in order to achieve the objectives stated above, are listed in table 4.4. The applications, as well as some advantages and disadvantages, of various types of bedrock samples are discussed in Butt and Smith (1979) and by Lovering and McCarthy (1977). Some of the more important aspects are noted in the following table.

Table 4.4. The application, advantages and disadvantages of the main types of bedrock samples.

1. Fresh whole-rock samples.

Application: The determination of background abundances of elements in an area; the recognition and mapping of geochemicaly specialized lithological units; the recognition of primary halos related to mineral deposits.

Advantages: A relatively small number of samples, selected on a geological basis, can give a large amount of information about the economic potential of an area and indicate the proximity of blind mineral deposits (under favourable conditions).

Disadvantages: Variations of trace element abundances in rocks unrelated to mineralization (e.g. due to modal variation, degree of fractionation, etc.) complicate the interpretation of analytical results; sophisticated processing of analytical results is often necessary to recognize primary geochemical halos due to low contrast and subtle variations of element abundances. The inhomogeneity of rocks can complicate representative sampling.

2. Altered whole-rock samples.

Application: Hydrothermally and metasomatically altered rocks can indicate the presence of buried mineral deposits genetically related to the alteration.

Advantages: Altered rocks define smaller targets than geochemical patterns in unaltered rocks; the trace element content of altered rocks can reflect the type and abundance of metals in genetically associated deposits.

Disadvantages: Alteration halos are generally small (except for porphyry deposits). Altered rocks tend to weather easily and leaching or enrichment of primary alteration halos in common.

Table 4.4. (cont.)

3. Vein fillings and fracture coatings.

Application: Vein fillings are an important sampling medium to detect leakage anomalies. Fracture coatings reflect secondary dispersion of elements by ground water. Both types are commonly collected as mineralized rock samples to indicate the type of metals present in an area.

Advantage: Vein fillings provide information on the possible channels followed by mineralizing fluids. The samples have particular application in carbonate rocks where other primary and secondary halos are generally of limited extent.

Disadvantages: The recognition of ore related fracture fillings and post ore secondary coatings; the widespread distribution of Fe and Mn (scavengers of trace elements) in fracture fillings.

4. Rock mineral separates.

Application: Trace element abundances in mineral separates can aid the recognition of geochemical specialization (Beus and Grigorian, 1977) and enhance primary geochemical halos. The partitioning of trace elements between rock forming minerals can indicate the types of ore and rock forming processes which operated in a particular geological environment.

Advantages: Mineral separates can be more selective indicators of mineralization than whole-rock samples.

Disadvantages: The use of mineral separates requires added sample preperation. The method has not been widely used in the past and its advantages and limitations have not been completely evaluated.

5. Weathered bedrock.

Application and advantages: Weathered bedrock may be the only viable sampling medium in areas with leached deep weathering profiles (i.e. soils and stream sediments may not reflect bedrock chemistry). The material can be used to indicate secondary dispersion patterns formed by weathering without the complication of physical dispersion.

Disadvantages: Outcrops in deeply weathered areas generally represent only resistant rock types and drilling and trenching are, thus, necessary for representative sampling. Mobile indicator elements tend to be removed from saprolite.

6. Gossans.

Application and advantages: Gossans are important surface indicators of a variety of mineral deposits (mainly Fe-rich sulphide deposits) which can be sampled to indicate the composition, size and grade of the deposit.

Disadvantages: The trace element abundances in gossans are highly variable due to leaching, scavenging by iron oxides, etc. Gossans are essentially ironstones and the recognition of true gossans from ironstones formed by weathering of barren rocks or sub-economic mineralization is often a problem.

The random sampling of fresh rocks, gossans and rocks showing signs of mineralization is a normal part of routine exploration work. The sampling is done in order to get an idea of the chemical characteristics of rocks and to establish the presence of the target elements in the exploration area. Lithogeochemical surveys, defined as the sampling and determination of the chemical composition of bedrock material with the objective of detecting distribution patterns of elements that are spatially related to mineralization (Govett and Nichol, 1979), can be carried out in areas with good outcrop.

a) Regional litholgeochemical surveys.

Widely spaced rock sampling on a regional scale can be carried out in order to detect geochemicaly specialized lithological units or areas (refer to section 2.2.0.). Routine sampling normally involves the collection of fresh whole-rock samples, from which specific mineral fractions may be separated if necessary. Geological control of the sampling (e.g. the sampling of specific types of rocks or lithological units) and adequate geological information about the area are essential in order to identify anomalies reflecting mineralization from those related to other causes. The collection of representative lithogeochemical samples is a further problem. Bradshaw et al. (1972) summarize the problem as follows:

> "While some rock types are relatively homogeneous making sample site selection and collection of representative samples easy, others are very heterogeneous making it virtually impossible to collect a sample representative of any petrographic unit except by very time consuming methods."

The sampling of ironstones on a regional scale appears to be an economical method of recogizing gossans related to sulphide mineralization. The interpretation of the surveys is, however, often difficult due to the chemical similarities between ironstones and gossans, and the variability of the chemical characteristics of gossans. The interpretation methods used and the difficulties encountered in a number of gossan surveys are summarized by Joyce (1976, pp 139 - 142). The case histories indicate that it is often advisable to drill all ironstone occurrences considered to be potential gossans, on the basis of geological and geophysical information, irrspective of the results of geochemical surveys.

b) Detailed lithogeochemical surveys.

Detailed lithogeochemical surveys, aimed at defining primary geochemical halos related to a specific mineral deposit, have important applications in the following situations (Govett and Nichol, 1979):

i) Local scale exploration to locate deeply buried and blind deposits.

ii) Exploration drilling to assist in drill hole location (e.g. sampling of shallow boreholes in order to define geochemical halos that can indicate the position of ore bodies).

iii) Mine scale exploration and underground mapping.

The variability of the primary geochemical halos associated with specific types of mineral deposits, due to variations in local geological and tectonic setting, prevents the definition of standardized sampling and interpretation procedures. Detailed lithogeochemical surveys have, thus, been most successful for locating further ore bodies in the vicinity of known deposits. A thorough understanding of ore forming processes and the local geology are essential for the application of detailed lithogeochemical surveys in new target areas.

5.0.0. ANALYTICAL FACTORS.

Ray's Rule for Precision: "Measure with a micrometer.
Mark with chalk.
Cut with an axe." (Bloch, 1980).

5.1.0. Analytical Procedures.

The concentration of an element in a sample may be estimated by a wide variety of analytical procedures which include wet analytical methods and instrumental analyses. Wet analytical methods involve colorimetric, gravimetric, volumetric and electrochemical measurement of the element by separating it in solution. Instrumental methods determine the quantity of an element in a sample by measuring some physical property of the element (e.g. emission spectroscopy, X-ray fluorescence, etc.). The principal methods of estimation and the minor elements for which they are commonly used are given in Table 5.1. Various analytical procedures involve some or all of the following operations viz. sample preparation, extraction, separation and estimation.

a) Sample preparation.

Sample of naturally occuring materials normally require some form of preparatory treatment before they can be analysed. The sample preparation may consist of any of the following procedures: drying, crushing, screening, splitting and grinding. The various procedures will depend on the type of material to be analysed and on the analytical procedure to be used. Special sample preparations (e.g. separation of a magnetic fraction, etc.) may also be required in order to achieve the objectives of the geochemical survey.

Sample preparation, if not correctly done, can result in significant analytical errors. The procedures involved in sample preparation are often time consuming and expensive resulting in a tendency to use compromise standard procedures which may result in significant contamination and sampling errors.

b) Extraction and separation.

Wet analytical methods and atomic absorbtion spectrometry, which generally requires the sample to be in solution before being aspirated into the instrument, require the extraction of the elements to be analysed from

Table 5.1A. Methods of estimation and minor elements for which they are commonly used. From Rose, Hawkes and Webb (1979).

Element	Colorimetry	Emission spectrometry d.c. arc	Emission spectrometry Plasma	Radiometry	Atomic absorption	X-ray fluorescence
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.

Table 5.1B. Comparison of analytical methods commonly used in exploration geochemistry. From Levinson (1974).

Name	*Cost of Equipment*	*Detection Limits (see Table 6-3)*	*Advantages*	*Disadvantages*	*Cost of Analysis in Commercial Laboratories*
Atomic Absorption	$4,000-20,000	Generally less than 10 ppm; some elements in ppb range	1. Rapid, sensitive, specific, accurate and inexpensive. 2. Several elements may be determined from same solution. 3. About 40 elements applicable to exploration geochemistry. 4. Partial or total analyses possible.	1. Accuracy suffers with high abundances. 2. Not satisfactory for some important elements such as Th, U, Nb, Ta and W. 3. Destructive.	1. Generally $1 per sample for first element, and 50¢ for each subsequent element determined on the same sample solution. 2. Au, Ag, Hg, Te, etc., from $1.50-$3.00. 3. Biogeochemical samples about twice regular rate. 4. Sample preparation (e.g. crushing, sieving) charges usually extra.
Colorimetry	Usually less than $1,000	Generally less than 10 ppm for elements commonly analyzed	1. Inexpensive, simple, sensitive, specific, accurate and portable. 2. Partial or total analyses possible.	1. Only one element (or a small group) determined at one time. 2. Not suitable for high abundances. 3. Some reagents unstable. 4. Tests not available for some important metals. 5. Destructive.	1. Generally 75¢ per element for cold-extractable. 2. Fusions or hot acid leaches generally $1.00 for first element, and 50¢ for each subsequent element determined on same solution. 3. Mo and W about $2.50 each.
Emission Spectrography	a. Visual detection $2,000-8,000 b. Photographic detection $15,000-30,000 c. Electronic (direct reader) $60,000-150,000	a. Usually only major and minor elements detected b. Generally from 1-100 ppm for most elements of interest. c. Same as (b) above.	1. Multi-element capabilities (for all instruments) 2. Only small sample required (for all instruments).	1. Complex spectra. 2. Requires highly trained personnel. 3. Generally slow (except for direct reader). 4. Sample preparation very critical and time consuming. 5. Destructive.	1. Qualitative or "semi-quantitative 30-element scans", $15-20. 2. Quantitative, about $5 for first element and $3 for each additional element on same film. 3. Direct-reader prices vary but probably about $30 for all elements recorded simultaneously.
X-ray Fluorescence	$30,000-40,000 (laboratory models)	50-200 ppm on routine basis; more sensitive with special procedures.	1. Simple spectra. 2. Good for high abundances of elements. 3. Uses relatively large sample. 4. All elements from fluorine to uranium are practical on modern equipment. 5. Certain liquids (e.g., brines) can be analyzed directly. 6. Excellent for rapid qualitative checks. 7. Non-destructive.	1. Sensitivities not as good as other methods for many elements. 2. Analyses slower than some other methods. 3. Analyses relatively expensive.	Generally $8-$12 per element per sample (quantitative); about half that price qualitative.

the sample material. Extraction may be accomplished by volatilization, fusion, vigorous acid attack, attack by weak aqueous extractants or by oxidation-reduction agents. The trace element being analysed may also have to be separated from interfering elements liberated during extraction. Atomic absorbtion spectrometry is the most commonly used method requiring extraction of elements into solution and has largely replaced the more exacting wet analytical methods for routine analyses.

The extent of extraction (incomplete or inconsistent extraction) and contamination (from reagents or equipment) are the major potential sources of error in the extraction and separation procedures.

c) Estimation.

The estimation of the element concentration of samples can be achieved by a large variety of techniques, many of which use highly sophisticated instrumentation. The sensitivity, precision and accuracy with which element concentrations can be estimated by laboratory instrumentation has made the use of semi-quantative field methods obsolete. Most commercial and private laboratories are capable of routine analysis of large numbers of samples for a variety of elements to levels of sensitivity and precision which satisfy the normal requirements of exploration geochemistry. The sensitivity and precision of instrumentation is, however, often negated by imprecision in the field and in other laboratory procedures (e.g. sample preparation).

A basic knowledge of the various techniques and types of instrumentation, particularly their advantages and limitations, is essential for the planning, execution and interpretation of geochemical surveys. Discriptions of the more commonly used methods given by Rose, Hawkes and Webb (1979), Levinson (1974 and 1980), Joyce (1976) and Stanton (1976) are recommended for field personnel as a basis for developing a working knowledge of the various techniques. The choice of the most suitable analytical procedure for a particular survey should, however, be made after consultation with the analyst. The analytical procedures available in the laboratory should be evaluated in terms of the objectives and problems of the geochemical survey. The important aspects of routine analysis which should be considered in the selection of an analytical technique are discussed in the following sections.

5.2.0. The Sensitivity, Precision and Accuracy of Analytical Results.

5.2.1. The limits of detection of analytical procedures.

The limit of detection (or sensitivity) is the minimum (and maximum) quantity of an element that can be measured by a specific analytical technique. The limit of detection varies depending on:

a) the analytical technique used.
b) the type and number of elements being analysed.
c) the matrix (material being analysed).

The limit of detection can not be exactly defined during routine analytical operations, but the approximate value for each element and each type of material analysed (e.g. granite rock samples or stream sediment samples from granitic terrane) by a particular analytical procedure should be established. The average concentrations in rocks, soils and sediments of the elements commonly used during geochemical exploration are in the range of 1 ppm to 100 ppm (Table 2.1 and Fig. 3.9) which is within the limits of detection of the commonly used analytical procedures. The lower limit of detection for the normal ore metals (e.g. Cu, Pb, Zn, Mo, etc.) during routine laboratory analysis is generally in the range of 1 ppm to 10 ppm. Elements with natural concentrations in the parts per billion range (e.g. Au, Ag) can not be readily detected by normal procedures and the use of these elements in exploration requires more sensitive techniques (e.g. neutron activation analysis).

The lower detection limit, which is defined as the concentration at which precision is ±100%, will influence the interpretation of surveys involving elements present in abundances close to the detection limit. Joyce (1976) summarizes the affects of the lower detection limit as follows:

a) The precision of all analytical procedures deteriorates near the detection limits. High values thus, have no significance if the true distribution of values isfairly constant and near the detection limit.

b) The "build-up" to anomalies will be masked if the general abundance of the element analysed is near the detection limit.

The upper detection limit is generally above the range of element abundances in commonly used sampling media, but should be investigated if very high concentrations of elements are being estimated.

5.2.2. The precision and accuracy of analytical results.

Precision is a measure of the reproducibility of replicate analyses without regard to how close their average is to the true value. Accuracy defines the closeness of the measured value to the true value. (Fig. 5.1.) The importance of determining the absolute content of an element in a sample depends on the nature and objectives of the geochemical survey. An accuracy within 10% of the true value of a given sample is generally acceptable, provided that the bias for different samples and different batches of samples from a particular survey is constant (e.g. case 2 in Fig. 5.1 would be acceptable if the difference between the analytical value and the true value was less than 10%). The precision of analytical data is dependent on the composit effects of field sampling, laboratory sampling and instrument errors. The precision of analytical results can have a major effect on the reliability and interpretation of geochemical surveys. Poor precision, even if bias is acceptable and constant, can mask geochemical anomalies or create false anomalies in the data. The effects of precision on interpretation are discussed in section 6.0.0.

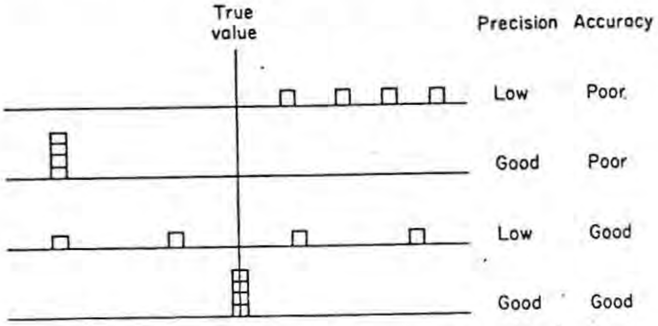


Fig. 5.1. Possible combinations of precision and accuracy based on four analyses of a sample. In case 3, only the average may be termed accurate. From Rose, Hawkes and Webb (1979).

The determination of the precision and bias of analytical results, discussed by Hatherley and Viewing (1981), Thompson and Howarth (1978), Garrett (1969) and Nicholls (1971), is essential for successful geochemical exploration.

a) <u>Determination of precision and bias in the laboratory.</u>

The procedure recommended by Viewing (1981) to establish analytical precision and bias, essentially involves:

1) Establishing a set of representative control samples for which a "known" value is determined by replicate analysis. (See Appendix 1).

11) Regular determination of the control samples and blanks during the routine analysis.

111) Statistical or graphical methods are used to determine bias which is a measure of the systematic error imparted during the analysis of a batch of samples, and analytical precision which represents the statistical or random error introduced by the analytical method used or by the instrumentation.

Batches of samples, in which the control samples show a +ve or -ve bias greater than 10% are re-analysed (Fig. 5.2). The differences between the expected and actual analytical results of the control samples (per batch) are used to calculate the analytical precision as follows:

Analytical precision at 95% confidence limits =

$$\frac{1{,}98 \times \text{Standard deviation}}{\text{mean}} \times 100\%$$

The analytical precision is used to evaluate the acceptablity of the analytical procedure and ±10% (or ±15%) is usually acceptable.

b) <u>Determination of sampling and analytical precision.</u>

The overall sampling and analytical precision is determined by taking replicate field samples. The recommended procedure is to collect duplicate samples at 10% of the sampling sites (with a minimum of 30) during the geochemical survey. The differences between the analytical results of the pairs of samples are used to calculate the combined

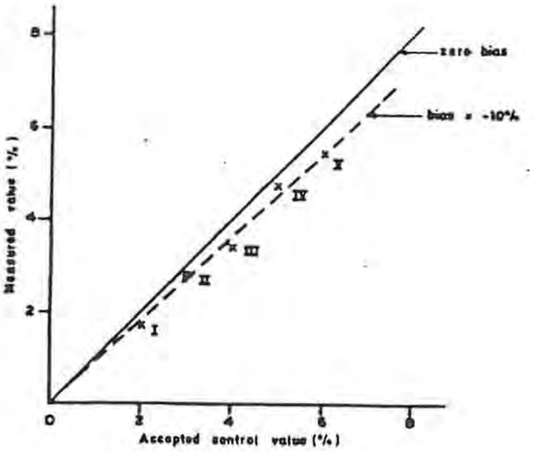


Fig. 5.2. Graphical determination of bias in a fictitious set of control samples.

sampling and analytical precision which is commonly expressed as follows:

Combined precision at 95% confidence limits =

$$\frac{1{,}98 \times \text{Standard deviation}}{\text{mean}} \times 100\%$$

The difference between the combined precision and the analytical precision (calculated from control samples) represents the field sampling precision of the project.

5.2.3. Total and partial extraction.

The "total" content of an element in a sample is normally used in geochemical exploration. Atomic absorbtion spectrometry, colorimetry and other wet analytical techniques are limited as "total" analytical methods by the extraction process used. The method of sample digestion routinely used in the laboratory can be affected by the occurence of the indicator elements in resistant minerals (e.g. magnetite) which are not completely digested by the reagents used. Various forms of partial acid digestion are generally used and elements not readily digested must either by analysed by a procedure not involving a digestion step or else the sample must be subjected to special digestion procedures. The person interpreting the analytical results should be aware of the extraction procedure used, and particularly the limitations of the procedure as far as the "total" digestion of various elements is concerned. It is advisable to state the extraction procedure and the reagents used in the geochemical project report.

The deliberate use of partial or selective extraction has advantages in the following situations (Rose, 1975):

1) Selective extraction can be used to investigate the form in which the anomalous constituents occur in a sample (e.g. in sulphides or adsorbed by Fe- and Mn-oxides). The information obtained can be used to understand the mechanisms of dispersion from mineral deposits and the controls of false anomalies.

11) Selective extraction can be used to plan special partial analytical approaches which optimize the contrast of anomalies, particularly in surveys where the orientation studies indicate that anomalies would show low contrast if conventional extraction was used.

Commonly used partial extraction techniques involve the use of dilute HCl, ammonium acetate solutions, EDTA solutions and other complexing agents which remove the readily extractable elements (e.g. adsorbed or weakly bonded elements). A knowledge of the characteristics of trace element distribution and bonding in the sample material can be of invaluable assistance in the choice of the optimum extraction technique. Rose (1975) described a number of selective extraction procedures which can be used to evaluate the form in which elements occur in a sample. The precision of partial extractions is dependent on temperature and other factors which affect the amount of the element extracted into solution. The usefulness of the various methods involving partial extraction, as well as "total" extraction methods, can be seriously limited by poor precision.

5.2.4. Factors affecting the reliability of analytical results.

a) Contamination.

The contamination of samples can occur at any stage from sample collection (or even before sample collection) until the element concentration in the sample is estimated. The greatest risk of contamination is in the laboratory, particularly during sample preparation and extraction. A large number of potential sources of contamination are, however, present in all phases of sampling and analysis. The following list is only an indication of some of the possibilities which should be avoided.

Sample bags (or other containers) with metal tags, staples or material empregnated with metals.

Metal sieves (especially brass).

Crushing and grinding equipment containing elements such as Fe, W, Co, Ni, Cr, etc.

The use of the same laboratory equipment for both ore grade and trace quantities of elements.

The use of contaminated reagents.

Dust (e.g. from mining activities, transport of ore etc.).

Metals from buildings, fences, bridges, etc.

Contamination from human activities (e.g. motor car exhausts, industry agriculture etc.).

Contamination can result in random or systematic errors, but the assumption that contamination from equipment (e.g. metal sieve) will result in consistent bias is not valid.

b) Sampling in the laboratory.

Reduction in grainsize, homogenization and controlled sample splitting are essential if the small portion of a sample to be analysed (generally less than 1 gram) is to be representative of the larger sample collected in the field. The effectiveness of a large field sample, taken to overcome natural variance of the material sampled, may be reduced to the effectiveness of a field sample of 1 gram if the sub-sampling in the laboratory is not representative. Nicholls (1971) investigated the affects of sampling precision in the laboratory. He found that the overall precision of the laboratory was dependent on the control of sampling precision, and that sampling imprecision often negated improvements in instrument precision.

The use of methods requiring the estimation of very low concentrations of elements in samples is becoming increasingly important in exploration. The estimation of very low concentrations of elements is particularly subject to the problems of non-representative sampling and contamination. The problem of laboratory sampling must, however, be veiwed in perspective, as the choice of an analytical procedure which has good precision can lose its benefit by not paying enough attention to representative sampling in the field. The precision required of the analytical procedure, which affects the cost and time involved in analysis, must be justified in relation to the variance attributable to field sampling.

c) Errors associated with the reporting of analytical results.

The recording of analytical results and associated information (e.g. sample locations, sample numbers, etc.) is subject to random and systematic error. Typographic mistakes can be a major source of error during surveys involving routine multi-element analysis of large numbers of samples. Plant (1980) quotes an examples of a regional survey (Table 5.2) where typographic errors formed 20% of the total error. Plant concludes that the locational errors can be reduced by digitizing the sample locations from field maps and that transcription errors can be eliminated by direct linking of analytical instrumentation with the computer in surveys using computerized interpretation and data storage.

Table 5.2. **Sources of typographic error in geochemical data processing (From 2000 samples from Orkney and Shetland)**

	percentage error
(1) recording National Grid Reference	**8.9**
(2) punching from field data cards	**1.2**
(3) plotting maps of sample sites	**5.2**
(4) digitizing sample sites from maps	**0.7**
(5) punching and sequence error in analytical data	**4.0**
total	**20.0**

From M. D. Forrest & R. T. Mogdridge (personal communication).

5.3.0. The Effect of Analytical Procedures on the Approach to Geochemical Exploration.

5.3.1. The selection of the type and number of elements to be determined.

The selection of the type and number of elements to be determined must be based on the objectives of the geochemical survey (i.e. on the type of mineral deposit sought). The following principals are suggested as a guide to the selection of the elements to be determined:

a) The target elements should be determined in all situations. In cases where the target elements are difficult and/or expensive to analyse routinely (e.g. Au, Ag) the entire exploration approach should be carefully evaluated (e.g. less, but more significant samples could be collected). An important reason for determing the target elements is to prove their presence in the exploration area.

b) Pathfinder elements, which have a meaningful and interpretable relationship with the target elements, can be determined. The extent to which the determination of pathfinder elements benefits the interpretation of the analytical results should be evaluated in terms of increased costs and the loss of sensitivity and precision in the determination of the target elements. The routine use of pathfinder elements in place of the target elements,because of apparently favourable characteristics such as ease and lower cost of determination, their presence in greater abundances in the sample material and their greater mobility in the geological and geomorphological environment, is not recommended. The approach should only be taken after serious consideration of the implications of not determining the target elements. The presence of pathfinder elements in an environment is not always an assurance of the presence of target elements.

c) Elements which indicate the presence of constituents in the sample material which affect the concentration of indicator elements (e.g. Fe and Mn in stream sediment and gossan samples) should be determined if orientation studies indicate that they can affect the selection of anomalous targets. Routine analysis of minor and major elements should be avoided as there is little value in knowing the iron content of a sample which contains no anomalous indicator elements. Re-analysis of samples containing significant concentrations of indicator elements for other elements which could have a bearing on the interpretation of the analytical results is the recommended approach.

d) The total and partial extraction of elements has already been discussed. Total extraction should be used for routine analysis, except for special cases indicated by orientation surveys where both methods should be used (see section 5.2.2.). Re-analysis of anomalous samples using partial extraction can often aid interpretation of geochemical results.

The selection of the type and number of elements to be determined has an important effect on the overall approach to a geochemical survey. Most private and commercial geochemical laboratories are capable of determining a wide range of elements, and the use of instrumentation capable of rapid multi-element determination is becoming increasingly popular. The routine use of multi-element analysis must, however, be evaluated in terms of cost, loss of precision and accuracy of determinations and the effect of the ability to generate large volumes of data on the approach to geochemical exploration.

5.3.2. Multi-element analyses of samples from high productivity regional geochemical surveys.

The availability of a range of sophisticated analytical techniques, which can routinely analyse samples for a large number of elements to acceptable standards of precision and accuracy at relatively low cost, has resulted in a trend towards the routine collection and multi-element analysis of large numbers of samples for geochemical mapping. The trend has been encouraged by the growth of computer technology and the increasing ability to manipulate large volumes of analytical results by computerized data analysis techniques.

The effectiveness of regional geochemical mapping, based on high productivity sampling designed to utilize the advantages of rapid automatic methods of analysis and computerized statistical techniques, is subject to severe limitations. Orientation studies on stream sediment sampling for a regional geochemical survey in Northern Scotland (Plant, 1971) indicated that two major problems may be encountered:

a) The procedural error could be too high to enable significant regional variation to be detected, other than in highly anomalous areas.

b) Variable bias introduced by secondary environment effects could be enhanced and further obscure the primary geochemical patterns.

The major factors which contribute to these limitations include

a) High productivity sampling from large areas is difficult to control and consequently the precision of field sampling is affected.

b) The preparation of large numbers of samples for analysis may result in a loss of precision which could negate the accuracy and precision of the analytical technique.

c) The logistics of the surveys require standardized procedures which limit the emphasis that can be placed on the geological and geomorphological factors affecting primary and secondary geochemical dispersion.

d) Orientation surveys can generally not be done in all the landscape situations present in the survey area and consequently the extent to which the samples are representative of the area from which they were collected is difficult to define and probably highly variable.

e) The computerized evaluation of the analytical results is often done without sufficient regard for the geological and geomorphological factors involved in the interpretation of geochemical surveys.

High productivity regional geochemical surveys should, thus, be carefully considered before they are used for mineral exploration. Plant (1971) summarizes the approach that should be taken as follows:

a) The identification of problems specific to the area to be investigated.

b) The design of a system to enable error to be controlled adequately at the sampling and analysis stages.

c) Prior confirmation that the regional variation is significantly greater than procedural error.

The cost of computerized statistical analysis of large volumes of geochemical data, the time and cost involved in interpreting the generally complex relationships in multi-element data, and the commitment to follow-up investigations of a large number of anomalies must be considered before a survey is undertaken.

5.3.3. The effects of analytical procedures with superior sensitivity and precision.

The availability of analytical procedures which can determine very low concentrations of elements (e.g. in the lower parts per billion range) has increased the potential of geochemical exploration. The full realization of this potential is, however, dependent on the extent to which the following requirements are met:

a) The ability to collect reliable and representative samples and to prepare the samples for analysis such that the analytical precision and sensitivity is not negated by the sampling procedures.

b) A prior knowledge of the type of mineral deposit sought as well as the type and nature of the elements most likely to indicate the presence of the deposit.

c) Sampling and analysis must be done with the objective of proving the existence of specific types of dispersion patterns which indicate the existence of a mineral deposit or indicate the potential of economic mineralization in an area. This requires that the geological and geomorphological factors affecting the characteristics of geochemical dispersion patterns in an area are understood, and that the analytical and sampling procedures are adapted to take advantage of specific types of dispersion patterns.

The advantage of increased precision and sensitivity has particularly affected the viability of lithogeochemical surveys which often require the detection of very low concentrations of elements. The principals involved are illustrated by the study of the extent and shape of wall-rock anomalies associated with two low grade hydrothermal gold veins conducted by Bolter and Al-Shaieb (1971). The determination of Au, Ag, Cu, Pb and Zn from carefully prepared rock samples indicated that the wall-rock anomalies for Cu, Pb and Zn (easily determined pathfinder elements) are of limited extent, while the gold and silver anomalies are more extensive (Fig. 5.3). Bolter and Al-Shaieb conclude that the precious metals might be useful for exploration if an accurate and sensitive analytical method (e.g. neutron activation) is employed.

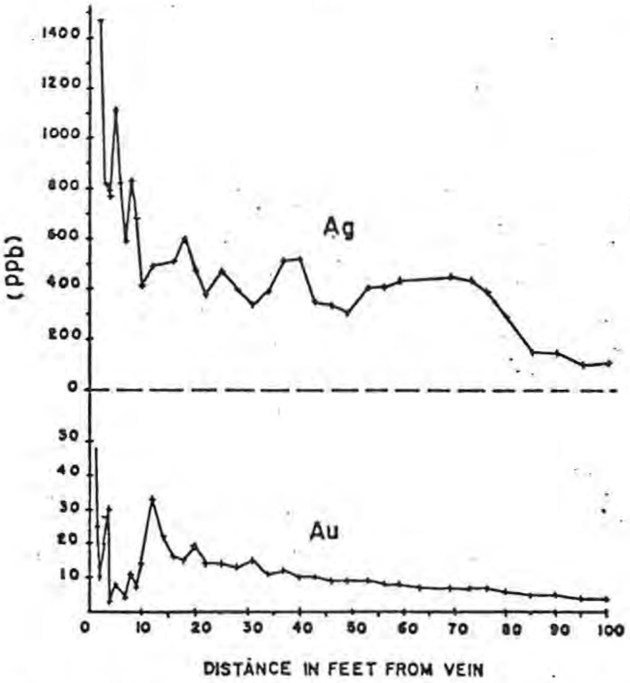


Fig. 5.3. Wall-rock anomalies associated with a low grade hydrothermal gold vein. From Bolter and Al-Shaieb (1971).

An overall approach to geochemical exploration which concentrates on the sensitivity and precision of analytical results is recommended. The approach has the advantage of forcing the people involved in geochemical exploration to evaluate the merits of every sample collected and analysed in relation to the objectives of the exploration effort.

5.3.4. The selection of an analytical procedure for a geochemical survey.

The choice of an analytical procedure depends on the objectives of the geochemical survey and on the geological and geomorphological factors affecting the primary and secondary dispersion of elements. The following factors should be considered when an analytical procedure is selected:

a) The mode of occurrence of the elements in the material to be samples.

b) The number and nature of the elements to be determined.

c) The sensitivity and precision required.

d) The economics and logistics of the operation.

Exploration companies with private geochemical laboratories should consider the affects of analytical procedures on the approach to geochemical exploration when laboratory systems are purchased. The situation where the availability of a particular analytical procedure in the laboratory dictates the exploration philosophy should be avoided. Rapid multi-element analytical techniques and sophisticated computerized data handling systems are particularly prone to encouraging a situation where the collection and analysis of large numbers of samples becomes the objective. The primary aim of locating an economic mineral deposit can easily be lost in a maze of analytical results.

6.0.0. THE PROCESSING AND PRESENTATION OF GEOCHEMICAL DATA.

> Fifth law of unreliability:
> "To err is human, but to really foul
> things up requires a computer." (Bloch, 1980).

6.1.0. The Basic Concepts involved in data processing.

6.1.1. The recognition of geochemical anomalies.

Joyce (1976) defines an apparent geochemical anomaly as a chemical abundance or dispersion pattern which is not readily explicable as having originated from barren rock types or their weathering products. The prefix "apparent" is generally omitted in practice. Abundances or patterns in geochemical data which have been proved to originate from mineralization are termed true geochemical anomalies, while those proved to originate from other causes are termed false geochemical anomalies.

The recognition of geochemical anomalies essentially involves two related operations:

1) The processing of analytical results, normally by the use of statistical techniques, in order to recognize samples with element concentrations which are not within the normal background concentration range for the material sampled. The definition of the normal background range requires the classification of samples into comparable groups on the basis of the geological and geomorphological factors affecting the interpretation of geochemical surveys (i.e. it is necessary to compensate for different background ranges associated with different rock types, weathering environments, etc.).

11) The compilation of analytical and field data, normally by plotting element concentrations, ratios, etc., on geochemical maps together with relevant geological and geomorphological information. The compilation involves the synthesis of analytical and field data in such a way that patterns in the data which could indicate the presence of mineral deposits can be recognized. The difficulty of recognizing patterns on raw data maps (e.g. figures plotted at sample locations on maps) requires the subdivision of numerical data into meaningful classes which can be represented on the maps or diagrams, such that distribution patterns inherent in the data are enhanced.

The processing of geochemical data normally generates a number of apparent geochemical anomalies, most of which are false. The processing must thus include attempts to eliminate false anomalies based on an understanding of the causes of the false anomalies and on real differences between the characteristics of false and true anomalies defined by orientation studies. The use of Pb, Zn, Mn and Fe to prospect stream sediments for Pb-Zn sulphide mineralization in manganiferous, sparodically lateritized rocks in agricultural terrane (Joyce, 1976) is an example in which it is possible to discriminate:

1) false Zn anomalies (e.g. fences, sheds, etc.) by the absence of associated Pb anomalies.

11) false Pb anomalies (e.g. shotgun pellets, car batteries, etc.) by the absence of associated Zn anomalies.

111) false Pb-Zn anomalies (attributable to scavenging by Mn and Fe enrichments) in which the abundances of Pb and Zn can be predicted by regression against Fe and Mn contents, and

1V) apparent anomalies in which Pb and Zn are both enriched and not explicable in terms only of scavenging by Mn and Fe.

The attempts to recognize and explain false geochemical anomalies should be aimed at reducing the incidence of expensive follow-up operations on false anomalies, without eliminating apparent anomalies which cannot be shown to be false within objective and reasonable limits of doubt. It is important, however, that all the apparent geochemical anomalies defined by the data processing are followed-up. The anomalies should be ranked during the processing such that those most likely to be true anomalies are followed-up first. The criteria which are applied to rank apparent geochemical anomalies are:

1) favourable geological location.

11) favourable size, shape and orientation.

111) contrast characteristics which are compatible with contrast encountered by analogous sampling for analogous targets in analogous terrane. This does not mean that samples showing the highest apparent contrast are necessarily the most significant samples for follow-up.

6.1.2. The choice of data processing methods.

The choice of a method to process the numerical and field data from a geochemical survey is dependent of three factors viz. the amount of data to be processed, the accuracy, precision and homogeneity of the analytical results and the expected contrast of true anomalies.

a) The volume of analytical and field data to be processed.

Geochemical surveys typically generate large volumes of numerical data. The use of descriptive statistics is the most objective and reliable method of condensing the numerical data and of extracting the information essential for interpretation. The amount of data to be processed should be estimated before a survey is undertaken so that statistical and other processing methods required to aid interpretation can be planned. The planned sampling design, analytical procedures and processing methods should be compatible.

The numerical data generated by geochemical surveys done during routine exploration programmes can generally be most reliably and cheaply processed by using simple statistical methods and maps compiled by the geologist responsible for the field work, who should also be responsible for the interpretation of the survey. The statistical calculations can be done manually, or by a computer directly linked to the analytical apparatus.

Computerized data handling systems are necessary for projects involving multi-element analysis of very large volumes of samples. The systems include procedures for classification, storing, statistical analysis and compiliation of analytical results and field data (Fig. 6.1). A large variety of graphs and geochemical maps (if sample locations are digitized) can be easily generated by the computerized systems. The difficulty of quantifying the large range of geological and geomorphological factors affecting the interpretation of geochemical surveys is a major draw-back of computerized data processing systems.

b) The accuracy and precision of analytical results.

The sampling and analytical errors which affect the precision and accuracy of analytical results cannot be corrected by statistical or other data processing methods, although a number of statistical techniques can be used to smooth the "noise" in numerical data. The sensitivity, precision and accuracy of the analytical results (see section 5.2.0.) is thus an important factor in the selection of a data processing technique. The use of sophisticated processing techniques is of little value if the inherent error in the analytical results is such that it can mask the natural variations and patterns in the element concentration of samples, which are used to recognize apparent geochemical anomalies.

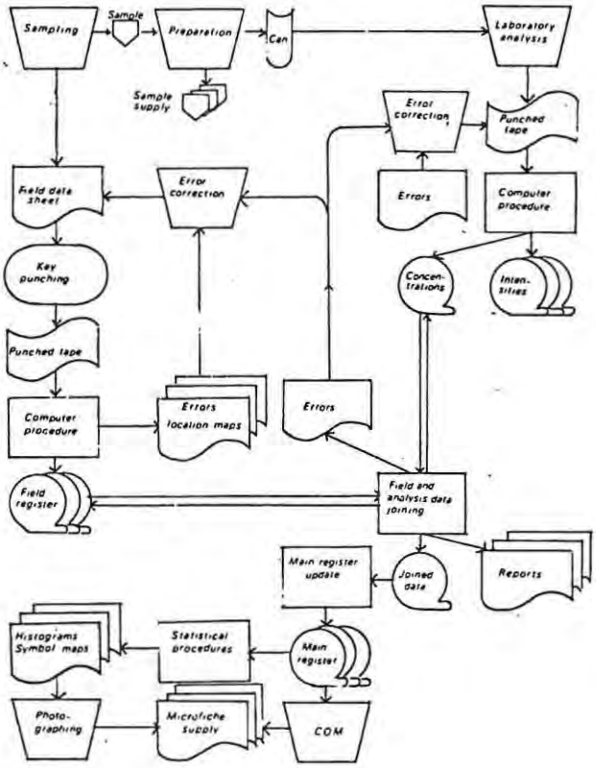


Fig. 6.1. A rough flow chart of a computerized data system. From Gustavsson in Kaurannee (1976).

c) <u>The expected contrast of true anomalies.</u>

The recognition of geochemical halos in which the indicator element abundance is only marginally higher than the normal background concentration is an important aspect of geochemical exploration. The expected contrast between background samples and anomalous samples should be established before routine sampling is undertaken. Simple data processing techniques are sufficient to recognize high contrast geochemical anomalies, but the chemical abundances and patterns indicating low contrast anomalies are difficult to recognize and tend to be masked by natural variations unrelated to mineralization. The ability to recognize low contrast anomalies can be improved by:

1) Increasing the contrast of anomalous samples by the manipulation of the numerical data (e.g. the use of element ratios).

11) Improving the precision and accuracy of analytical results.

111) Selecting the sample medium and analytical procedure which gives the highest contrast.

The recommended approach during geochemical surveys forming part of normal exploration programmes is to concentrate on improving the sampling and analytical aspects which can affect the recognition of low contrast geochemical halos. Sophisticated techniques of data manipulation should only be used if the simple processing methods still fail to clearly define low contrast anomalies with improved sampling and analysis.

6.2.0. The Statistical analysis of Geochemical data.

6.2.1. Probability graphs.

Probability graphs are a simple and effective method of analysing geochemical data in order to define statistical features of the numerical data which can aid the interpretation of geochemical surveys. Various types of probability graphs can be used to:

1) Recognize the existence of one or more populations in the data for each element.

11) Separate the data for each element into its constituent populations and determine the threshold values which delineate these populations. The simplest case is the use of probability graphs to distinguish mineralized samples from unmineralized samples.

111) The type of statistical distribution of the data in the various populations can be determined (in practice it has been found that geochemical data is generally log-normally distributed).

1V) The average value and an expression of the degree of variation around the average can be determined for the various populations.

The common types of probability graphs used for the analysis of geochemical data are shown in Fig 6.2. The construction and interpretation of the probability graphs is discussed by Lepeltier (1969), Sinclair (1976) and Hatherley (1978). Some of the more important aspects are briefly discussed below, but the references cited should be consulted for detailed discussion.

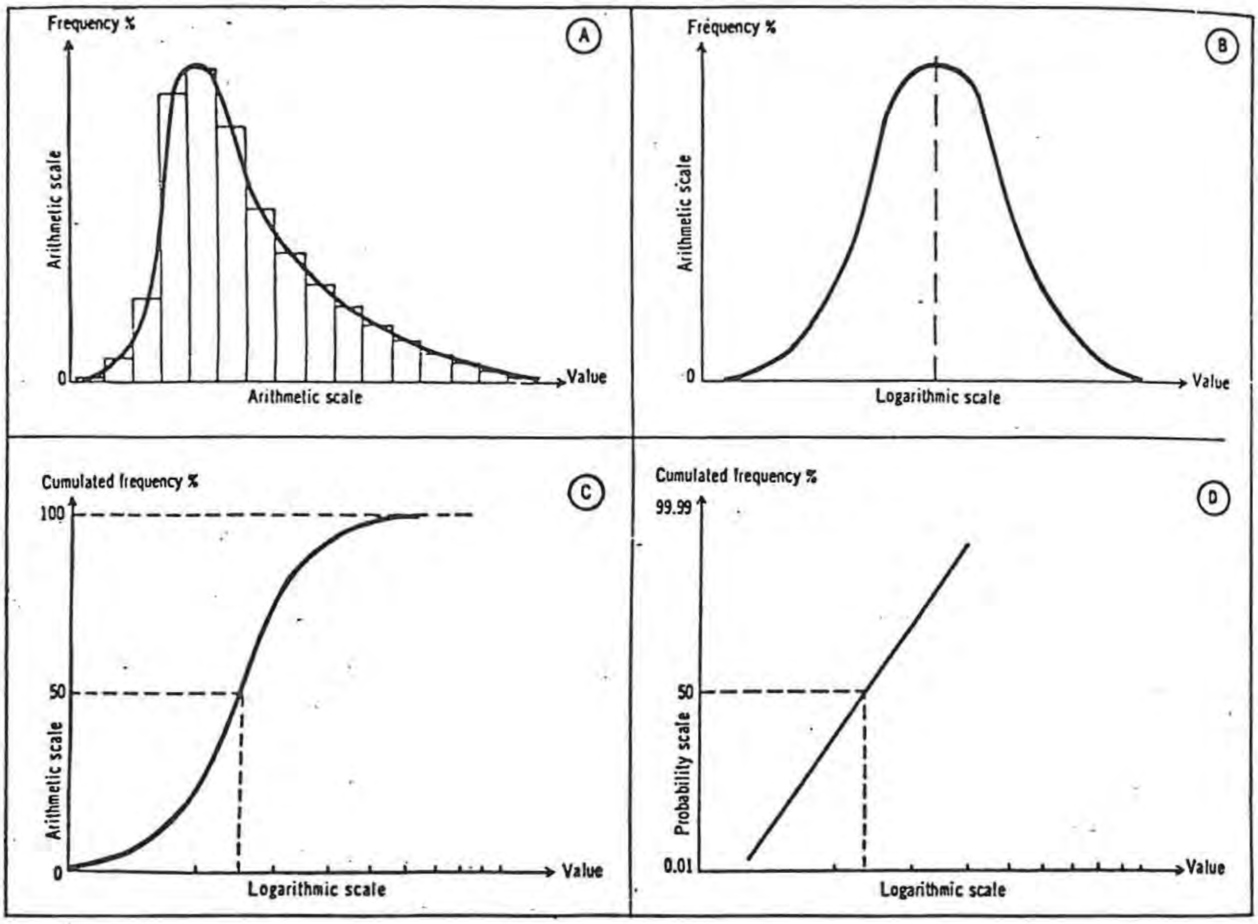


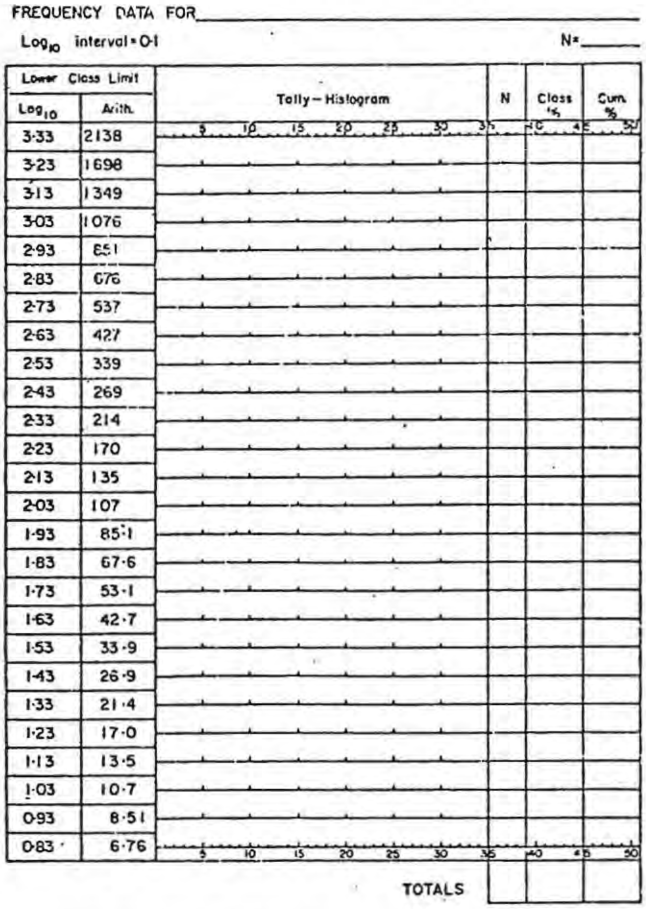
Fig. 6.2. Lognormal distribution curves. (A) Histogram and frequency curve. (B) Lognormal distribution with concentration plotted on a logrithmic scale. (C) Cumulative frequency curve. (D) Log-probability cumulative frequency plot. From Lepeltier (1969).

a) Classification of samples.

The samples must be classified into homogeneous groups (e.g. on the basis of lithological units) and the analytical results from each of the groups of samples must be treated separately during statistical analysis. The groups of samples should be as large and homogeneous as possible in order to get more precise and reliable results, although as few as 70 values can give meaningful probability graphs (Sinclair, 1976).

b) <u>The grouping of numerical data into class intervals</u>.

The correct grouping of numerical data for each element from a particular group of samples into class intervals is necessary for the construction of probability graphs. Too few class intervals result in the loss of important features of the populations distribution, while too many classes tend to give erratic distributions which mask the significant inflection points. Shaw (1964, quoted in Sinclair, 1976) recommends that the class interval used should be between 0,25 and 0,5 of the standard deviation of the data and that 15 to 25 class intervals are normally adequate for the statistical analysis of data.



FREQUENCY DATA FOR ______

Log_{10} interval = 0·1 N= ______

Lower Class Limit		Tally – Histogram	N	Class %	Cum. %
Log_{10}	Arith.				
3·33	2138				
3·23	1698				
3·13	1349				
3·03	1076				
2·93	851				
2·83	676				
2·73	537				
2·63	427				
2·53	339				
2·43	269				
2·33	214				
2·23	170				
2·13	135				
2·03	107				
1·93	85·1				
1·83	67·6				
1·73	53·1				
1·63	42·7				
1·53	33·9				
1·43	26·9				
1·33	21·4				
1·23	17·0				
1·13	13·5				
1·03	10·7				
0·93	8·51				
0·83	6·76				
		TOTALS			

Fig. 6.3. Example of a tally sheet for field use in preparing probability graphs. From Sinclair (1976).

The appropriate interval for a set of geochemical data to be evaluated by the use of cumulative frequency curves can be estimated as follows (Lepeltier, 1969):

$$\text{Log (interval)} = \frac{\text{Log } R}{n}$$

where R = the ratio of the highest to the lowest value in the data.

n = the number of class intervals (Lepeltier recommends the use of between 9 and 19 classes).

Sinclair (1976, pp 84 - 86) describes a rapid method of grouping data into classes and calculating the frequency of occurrence in each class for the field application of cumulative probability plots. The method is based on the construction of a simple table (e.g. Fig. 6.3) by rounding-off the class interval calculated as above and setting up classes starting at an odd number to avoid the problem of value coinciding with class boundaries.

c) The advantages of the various types of probability graphs.

Hatherley (1978) tested the different methods of separating populations and determining threshold values in a set of geochemical data. He concluded that:

1) The best methods of displaying geochemical data are by means of the log-probability cumulative plot or by 15 to 30 cell histograms which may be smoothed by the use of moving averages.

11) The intermediate cumulative plots (e.g. Fig 6.2.) do not aid in the interpretation and the threshold values determined from them are often unreliable.

111) The mathematical approach to the separation of the constituent populations in a set of numerical data (Sinclair, 1976) is not always necessary. Graphical methods are generally sufficiently accurate, particularly if the inflection points are clearly defined.

6.2.2. Statistical methods based on the covariation of multi-element data.

The sympathetic and antipathetic covariation of multi-element data can give added information for the interpretation of geochemical surveys. A variety of simple graphical and more complex mathematical methods can be used to determine and analyse the covariation of two or more variables. The use of the methods to aid the interpretation of geochemical surveys must be based on the recognition of natural relationships in the geochemical data which can be used to indicate the presence or absence of mineral deposits. The use and advantages of some of the more common methods, described by Joyce (1979, pp 79 - 88) are briefly listed below.

a) Element ratios.

Element ratios are a simple method of combining two or more variables into a single derivative variable. The use of element ratios can be illustrated by the following examples:

1) The determination of the ratios of trace and major elements which vary sympathetically in order to derive a combined distribution pattern (e.g. the ratio of Cu:Fe could be used to eleminate false anomalies caused by the scavenging of Cu by iron oxides).

11) The ratios of target and pathfinder elements can be used to enhance anomalies associated with mineral deposits (e.g. ratios involving Ni, Cu, Co and Zn can be used to separate Ni anomalies associated with magmatic sulphides, which have high Ni, Cu, Co and low Zn, from false anomalies related to concentrations of Ni and Zn in the silicate minerals of ultrabasic rocks).

111) Beus and Grigorian (1977, chapter 5) describe the use of element ratios to interpret zoned lithogeochemical halos and predict the position of blind hydrothermal deposits.

1V) Ratios of geochemically associated elements can be used to indicate the geochemical specialization of rocks (Beus and Grigorian, 1977, pp 60 - 66).

b) Discriminant analysis.

Discriminant analysis can condense a number of variables into a single variable (discriminant score) which can be used to separate populations not readily divisible on the basis of single element data.

c) Cluster analysis.

Cluster analysis can be used to condense a confusingly large array of data into a simplified form in which similarites and even quite subtle dissimilarities of both samples and variables can be recognized. The simplest method of cluster analysis involves the construction of a scattergram to seek natural groupings of samples on the basis of two variables (e.g. Fig. 6.4.)

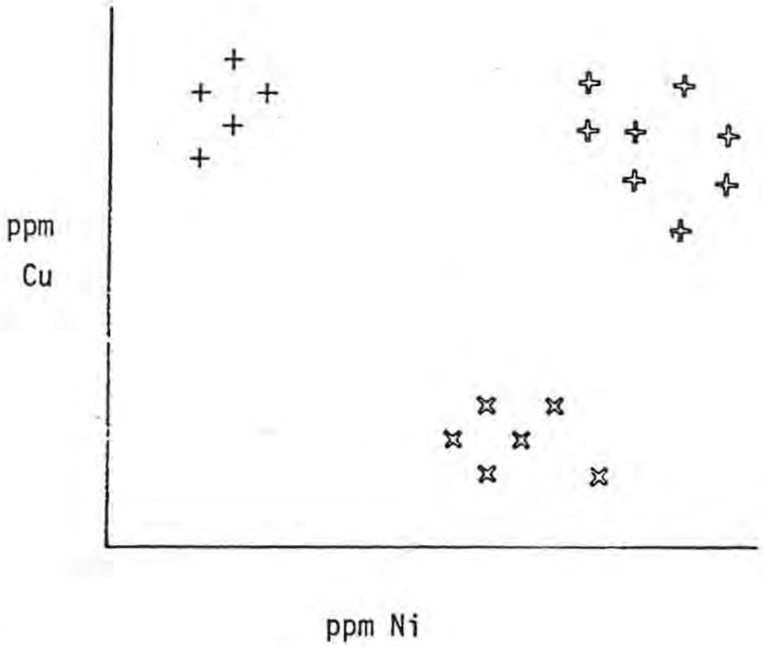


Fig. 6.4. Scattergram of Cu versus Ni showing three clusters of samples. From Joyce (1976).

The use of more than three variables to determine clusters of samples can only be done mathematically. Q-mode cluster analysis calculates a linear distance function representing the amount of separation of two sample points in multidimensional space. R-mode cluster analysis reverses the roles of samples and attributes in order to define the covariation of the attributes (e.g. the covariation of Zn with other elements in multi -element data). The results of both Q- and R-mode cluster analysis are normally presented on a dendogram and their main applications in exploration are:

1) Q-mode analysis to classify small batches of samples into natural groups (e.g. Fig. 6.5.).

11) R-mode analysis of sets of control samples from a multi -element survey to establish the natural association of elements and thereby deduce the dispersion mechanisms involved. Indicator elements useful for portraying the distribution of various sample attributes (e.g. genetic types of mineralization, contamination, lithology types, etc.) may be recognized.

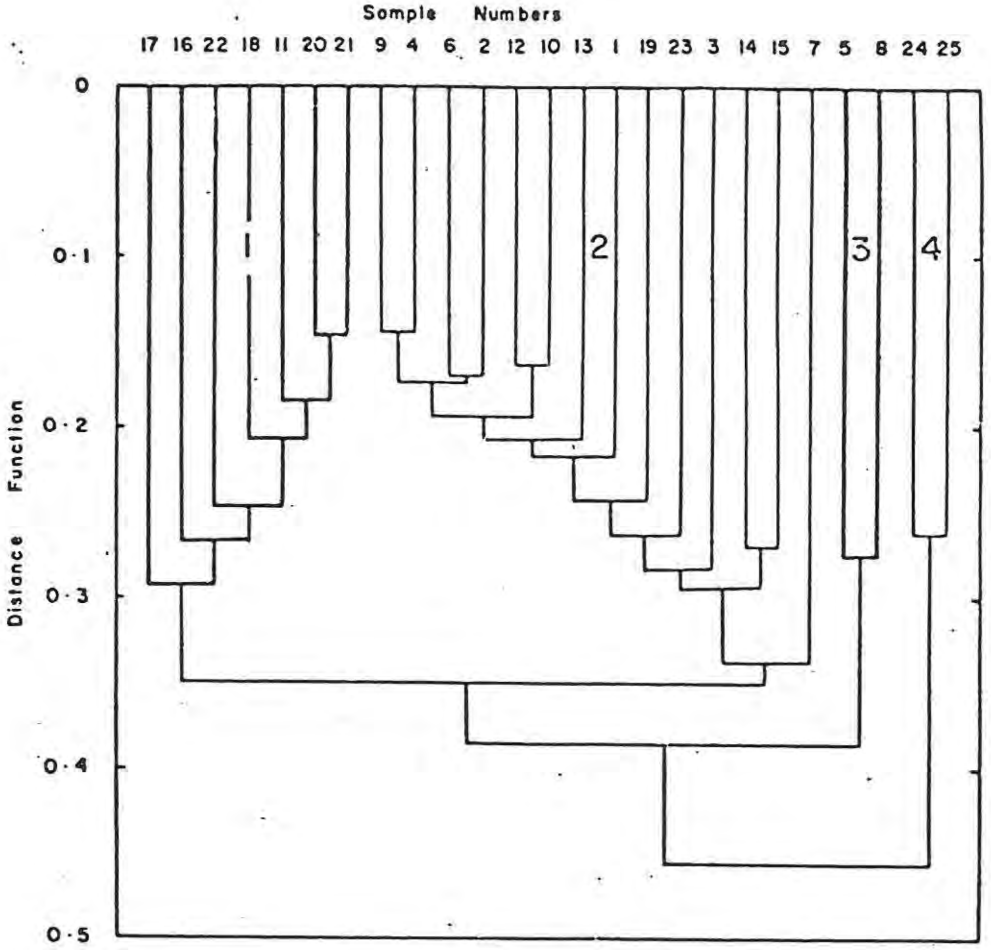


Fig. 6.5. Typical dendrogram derived by Q-mode cluster analysis. From Joyce (1976).

d) Principal component and factor analysis.

R-mode and Q-mode principal component and factor analysis are also mathematical techniques which can aid the interpretation of multi -element geochemical surveys.

1) R-mode principal component analysis can be used to establish chemical variables which behave with sufficient similarity to allow their combination into a new variable (i.e. the principal component of variation). The method can be modified to classify samples by calculating principal component scores for individual samples relative to the new variables (i.e. the components of variation).

11) Q-mode principal component analysis searches for similarities

between samples rather than elements by measuring the angles between pairs of samples plotted in multidimensional space.

111) Factor analysis is derived from R- or Q-mode principal component analysis by rotating the principal component vectors in space according to some specified mathematical criterion designed to achieve a specified objective (e.g. maximizing the variance).

e) Multiple regression analysis.

Multiple regression analysis can be used to establish unique background concentrations for each sample collected in a survey by defining a linear equation which relates the abundance of indicator elements to easily measurable causes of variation (e.g. the abundance of Fe, Mn and organic scavengers, changes in pH, etc.). Discrepancies between measured and predicted abundances of indicator elements can be plotted on deviation maps which aid the recognition of geochemical anomalies unrelated to the measurable causes of variation.

6.2.3. The application of statistical procedures to aid the interpretation of geochemical data.

The application of statistical methods in geochemical exploration whould be based on an understanding of the aims, constraints and results of the procedures in order to select procedures that satisfy the requirements and objectives of the geochemical survey. In general, the simple statistical methods (e.g. probability graphs, scattergrams, regressions, etc.) should be used to aid the initial interpretation of geochemical data. The use of more complex statistical methods should be considered in situations where orientation work and experience indicate that the basic methods will not be capable of discriminating apparent anomalies from background or eliminating a satisfactory proportion of false anomalies. The selection of an appropriate statistical approach to aid the recognition of particular aspects of data, in the situations where basic statistics are considered inadequate, should be deliberately planned, in consultation with a competent statistician, before the routine sampling is undertaken. The potential usefulness of various statistical approaches to particular types of geochemical problems is illustrated by the references in the selected annotated bibliography compiled by Joyce (1976, pp 100 - 114).

6.3.0. The Synthesis, Compilation and Presentation of Analytical and Field Data.

6.3.1. Geochemical maps.

The final interpretation of geochemical data always requires consideration of the geographic and geological location of samples. Two aspects of the location of analytical results are important:

1) The spatial distribution of analytical results can be used to recognize linear or areal variation trends in the data.

11) The quality of the location of a sample with anomalous element concentrations can be evaluated by plotting the analytical results on maps showing relevant geological and geomorphological information compiled from field data.

The advantages of location as an extra variable are best utilized by plotting geochemical maps. The type of map or diagram plotted is dependent on the characteristics of the analytical and field data available, but the basic types of geochemical maps, discussed below, are normally sufficient for the interpretation of geochemical surveys aimed at defining target areas at locating anomalies associated with individual mineral deposits.

a) Geochemical base map.

Geochemical surveys can only be successfully interpreted if the analytical results are considered within the context of the geological and geomorphological features of the exploration area for the following reasons:

1) Mineral deposits of economic significance are produced by a favourable combination of geochemical and geological factors.

11) Characteristics such as the size, shape, intensity and contrast of geochemical halos (and therefore the characteristics of geochemical anomalies) associated with mineral deposits are largely dependent on the local geological and tectonic setting (as discussed in section 2.0.0.).

111) The characteristics of surficial geochemical dispersion patterns are dependent on the dynamic interaction of surficial processes controlled by a variety of environmental factors (as discussed in section 3.0.0.).

The compilation of geochemical base maps which synthesize the geological and geomorphological factors affecting the interpretation of geochemical surveys should emphasize features relevant to the type and scale of the geochemical survey (e.g. the distribution of soil types is important for the interpretation of detailed soil survyes, but does not influence the interpretation of regional stream sediment surveys). The selection of the relevant information to be plotted on the maps must be based on:

1) Orientation surveys.

11) Geological and geophysical surveys forming part of the overall exploration programme.

111) Theoretical considerations of factors such as the ore forming processes, element mobility, the tectonic and geological setting of mineral deposits, etc.

b) Raw data maps.

Analytical results (e.g. p.p.m. values for each element analysed) should be plotted adjacent to points representing sample localities on copies of geochemical base maps or on transparent overlays. Copies of raw data maps are useful for the compilation of coded geochemical maps and for use as field maps. The raw data maps are a good method of filing analytical results for future reference as numbers on lists of data are meaningless without a reference map. Computer filing should be considered if large volumes of analytical and field data are involved, but the system should make provision for recovering the information as raw data maps.

c) Coded geochemical maps.

Local populations and patterns are not conspicuous on raw data maps and particular ranges of geochemical values can be coded in order to make apparent geochemical anomalies and other patterns in the data easier to recognize by simple inspection of the maps. The selection of intervals for coding raw and processed (e.g. element ratios) geochemical data should be based on meaningful subdivisions (e.g. the threshold values separating various populations in the analytical results). The precision of the analytical results has an effect on the reliability of boundary values and is an important factor affecting the selection of meaningful ranges for coding geochemical maps (e.g. Table 6.1. and Fig. 6.6).

Table 6.1. Effect of analytical precision upon a range of concentration. From Viewing (1981).

Increment	Range	+ 10%	- 10%	Range	Overlap
100	50 - 150	55 - 165	45 - 135	45 - 165	-
100	151 - 250	166 - 275	136 - 225	136 - 295	29
100	251 - 350	276 - 385	206 - 315	226 - 385	49
100	351 - 450	386 - 495	316 - 405	316 - 495	69
100	451 - 550	496 - 605	406 - 495	406 - 605	89

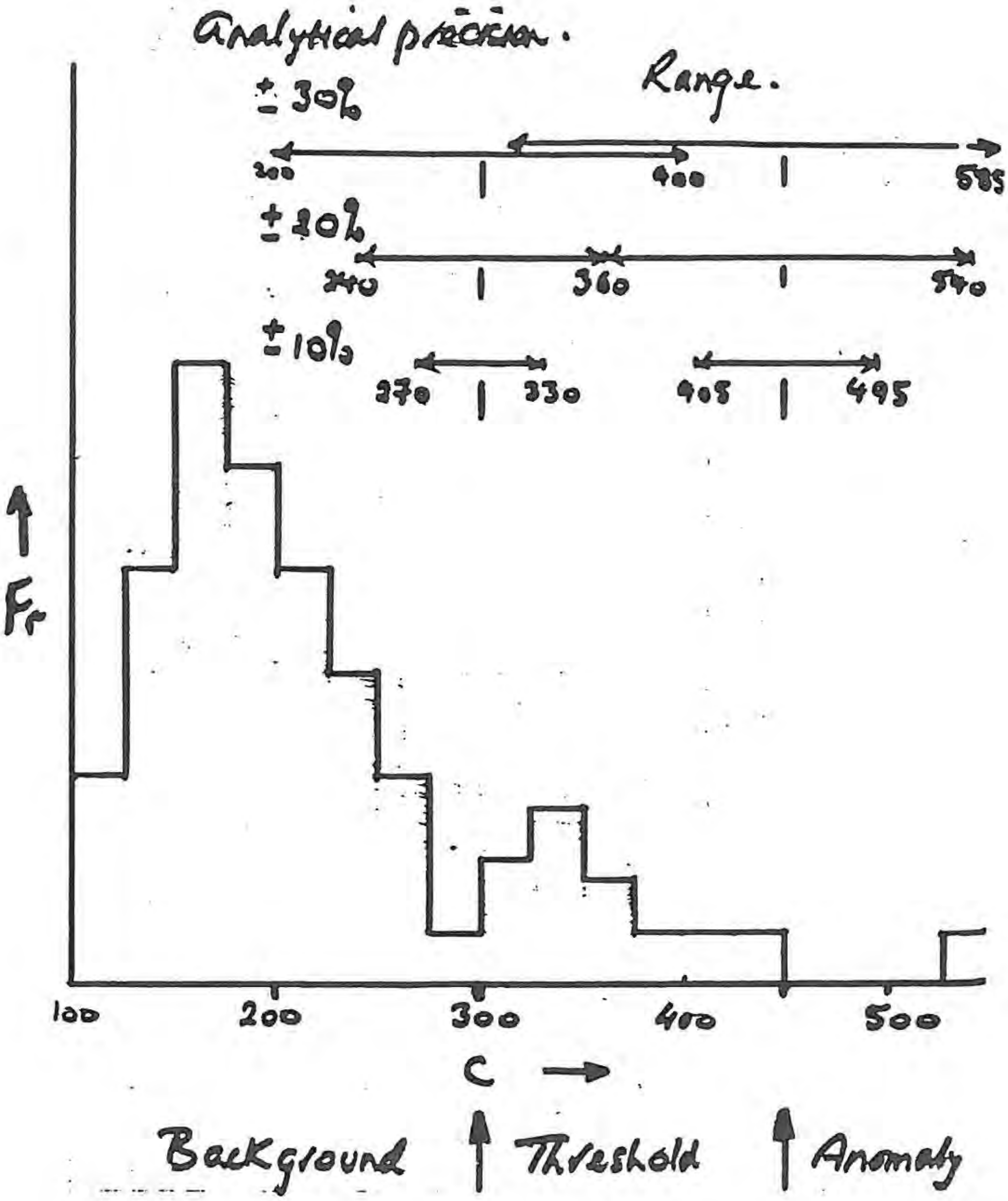


Fig. 6.6. The effects of analytical precision on boundary values. From Viewing (1981).

The selection of a coding system depends on the type of geochemical survey, the sampling design and the scale of the geochemical maps. The coding systems that can be used to aid the interpretation of the more common types of geochemical surveys are:

1) The coding of regional geochemical surveys is best accomplished by using symbols plotted at the sample points on geochemical base maps. The size and/or the design of the symbol is used to represent a selected concentration range or processed data values (e.g. samples grouped by cluster analysis). The superimposition of the symbols on raw data overlays (i.e. maps on which the actual element concentrations are plotted) is recommended.

11) The contouring of geochemical data is a useful aid to interpretation as the contours emphasize patterns in the data. The inspection of shaded contour maps facilitates a mental moving averages analysis of the data (i.e. higher element abundances in areas of low background are easily recognized, even if the anomalous abundances are low compared to the total range of abundances encountered in the survey area).

The sampling design, particularly the sample spacing and density, places limitations on the use of contouring to code geochemical maps. The method is best suited to aid the interpretation of detailed grid surveys in which the sampling density is sufficient to show the patterns sought and in which the analytical results are representative of the influence area of the samples. The contouring of detailed soil or lithogeochemical surveys can, thus, emphasize important characteristics (e.g. size, shape and orientation) of geochemical anomalies associated with individual mineral deposits, while the contouring of regional stream sediment surveys can only delineate broad geochemical patterns.

111) Computerized coding (e.g. grey shading, symbols, etc.) can aid the interpretation of broad geochemical patterns (e.g. lithological units) in regional multi-element geochemical surveys. The coding can be used to depict a variety of computer derived values (e.g. element ratios, regional patterns smoothed by moving averages analysis, etc.).

d) Line profiles.

Line profiles (i.e. graphs depicting element abundance versus sample location) can be used to represent data on widely spaced traverses with close sample spacing. The use of line profiles to replace other methods of depicting geochemical data on maps is not recommended as the profiles tend to emphasize variation in one direction only and areal patterns in the data are masked. Erratic line profiles are difficult to interpret (particularly between traverses). The tendency to smooth the graphs for easier plotting and interpretation can give a misleading impression of regular variations in element abundance.

Line profiles, plotted as separate diagrams, are a useful aid for the interpretation of detailed stream sediment surveys as anomalous element abundances in the streams tend to decrease regularly with stream distance from the anomaly source. Background element abundances also tend to decrease regularly with distance downstream and regression lines or curves can thus be used to recognize anomalous dispersion trains.

6.3.2. Conceptual geochemical model.

The interpretation of geochemical surveys requires a system of evaluating the effect of the interaction of the lithosphere, hydrosphere, atmosphere and biosphere, during geological time, on the mobility and distribution of indicator elements in the surficial environment. Landscape geochemistry (Fortesque, in Bradshaw, 1975) offers a framework in which all the components of the surficial environment can be treated together. Landscape geochemistry involves the development of a three dimensional model of the surficial environment and the geochemical patterns developed under a defined set of conditions. Three classes of models viz. field level, tactical level and strategic level, can be constructed.

a) Field level models include diagrams of landscape prisms, landscape sections and block diagrams drawn to scale on the basis of field observations. The aim of the models is to aid the interpretation of individual geochemical anomalies.

b) Tactical level models are similar scale diagrams which have been generalized from field level models in order to clarify the display. The models should be used to synthesize data from a geochemical survey for presentation in reports.

c) Strategic level models are landscape diagrams, not drawn to scale, in which information from a number of sets of field data is generalized. The diagrams are used to emphasize the mechanisms of migration and factors controlling the use of geochemistry which are common to a particular type of landscape.

6.3.4. The presentation of geochemical data.

The presentation of geochemical data is primarily aimed at facilitating decisions on the follow-up of a particular geochemical survey. The presentation should, however, also aim to synthesize the geochemical data in a form that can be easily evaluated at a later stage under different circumstances and with additional information. The following aspects of data presentation are important in order to achieve these aims:

1) The major factors which affected the interpretation of the data and influenced the selection of apparent geochemical anomalies should be clearly defined.

11) The sampling, analytical and interpretation methods used should be indicated on maps and diagrams, and described in the report on the survey.

111) The confidence limits placed on the interpretation should be clearly defined (e.g. the sampling and analytical precision must be indicated on geochemical maps).

1V) The recommended follow-up procedures should be indicated.

V) The maps, diagrams and reports should be easy to reproduce and should be meaningful when reproduced without requiring further work.

7.0.0. CONCLUSIONS AND RECOMMENDATIONS

> Spencer's laws of data:
> "1. Anyone can make a decision given enough facts.
> 2. A good manager can make a decision without enough facts.
> 3. A perfect manager can operate in perfect ignorance."
> (Bloch, 1980).

a) The geological and geomorphological factors responsible for natural variations of the geochemical characteristics of various types of mineral deposits and the primary and secondary halos associated with them are the most important factors affecting the interpretation of geochemical surveys. Interpretation must thus be based on a thorough knowledge of the characteristics of mineral deposits, the geological and tectonic processes involved in their formation, and the tectonic, geological and geomorphological processes which alter the primary characteristics of the deposits.

b) The deliberate planning and execution of geochemical surveys with the objective of locating a specific type (or types) of geochemical halo associated with a specific type of mineral deposit is essential for the successful interpretation of the survey. The geological, geomorphological and geochemical characteristics of the exploration area must be considered in order to select sampling and analytical procedures which can simplify the interpretation process and still achieve the objective of the survey. Orientation surveys are essential for the objective evaluation of the factors affecting the design and interpretation of geochemical surveys.

c) Sampling and analytical errors, which affect the reliability of analytical results, are a major factor affecting the confidence with which geochemical surveys can be interpreted. The accuracy and precision of modern analytical instrumentation, which are generally satisfactory for the purposes of geochemical exploration, can be negated by sampling errors in the field and the laboratory. Sampling errors can only be reduced by the use of field and laboratory techniques which concentrate on the quality of each sample. High productive sampling programmes which concentrate on the collection of large numbers of samples by standardized procedures are not recommended as they tend to defeat the objectives of reliable sampling and analysis.

d) The choice of indicator elements to be determined during routine analysis is a critical factor affecting the interpretation of geochemical surveys. The target elements and closely associated pathfinder elements are the most reliable indicators of mineralization. The standardized use of multi-element analysis is not recommended as it avoids the deliberate evaluation of the best indicators of mineralization. The primary objective of discovering a mineral deposit can easily be lost in the maze of analytical results generated by high productivity multi-element surveys.

e) The successful interpretation of geochemical surveys requires the synthesis of analytical and field data and information from geological and geophysical surveys forming part of the overall exploration programme. The selection and compilation of relevant information and the interpretation of the geochemical survey should be done by field geologists intimately involved in the overall exploration project.

f) Many of the geological, geomorphological, sampling and analytical factors affecting the interpretation of geochemical surveys are applicable on a regional scale. The information and experience gained from the empirical interpretation of individual geochemical surveys is, thus, a valuable asset to the exploration company and should be preserved for future use. Tactical and strategic level conceptual geochemical models relevant to the operational areas of the exploration company are recommended as an economical and useful method of preserving the information and experience gained from individual geochemical surveys.

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APPENDIX 1.

RECOMMENDATIONS FOR THE CONTROL OF ROUTINE ANALYSES IN THE GEOCHEMICAL LABORATORY - Prof. K.A. Viewing (1981), Geochemical exploration course notes, Rhodes University.

A series of standard control samples and blanks can be used to identify errors due to operators, instruments, reagents and contamination from other sources. Ideally, these samples are made from natural materials, rock samples or stream sediments from the areas in which prospecting is in progress. The sample should contain metals in the ranges which are expected to occur in prospecting.

The standard control samples are made up according to the following recommendations:-

(i) Determine optimum size fraction for analysis.

(ii) Collect say 25kg of sample from an anomalous area and 25kg from a background area.

(iii) Sieve this material and discard the oversize.

(iv) Analyse the bulk high and bulk low samples 30 times for each sample. Obtain the arithmetic mean value. The spread of values for the high and the low sample should be less than ± 15% of the mean.

(v) Weigh proportions of the bulk high and low so as to obtain 10 samples.

Sample No.	1	2	3	4	5	6	7	8	9	10
Proportion high %	100	90	80	70	60	40	30	20	10	0
Proportion low %	0	10	20	30	40	60	70	80	90	100

(vi) Split the bulk high and low samples and mix the intermediate samples in a tumbling container, say a clean 10 litre or 20 litre polythene bottle, for 2 hours until it is believed to be thoroughly mixed. Mixing can be achieved best by rolling and tilting end over end.

(vii) Analyse these samples and plot according to Fig. 1 . All of the values should be less than ± 15% of the mean.

(viii) Introduce these samples, not necessarily in order, at intervals of one control to 10 or 20 of the unknowns, so that at least one batch of 10 control samples is analysed each day, in addition to one blank sample per 100 samples.

(ix) Determine the analytical precision for the batch and report on the analytical results sheet with the data.

(x) Repeat any batch of analyses in which the control samples show a value of greater than ± 20%.

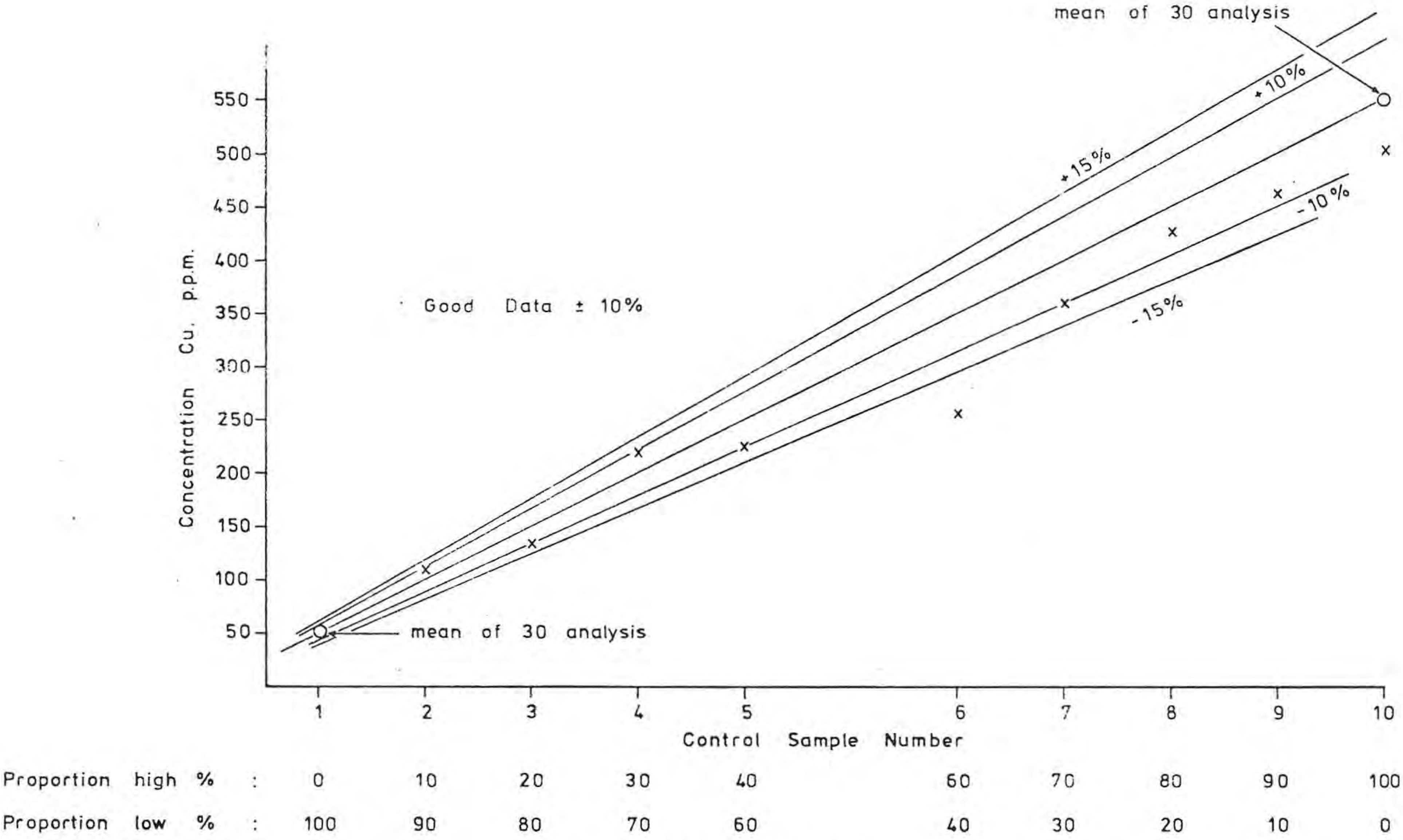

Fig. 1. Standard Control Samples : Copper Hx

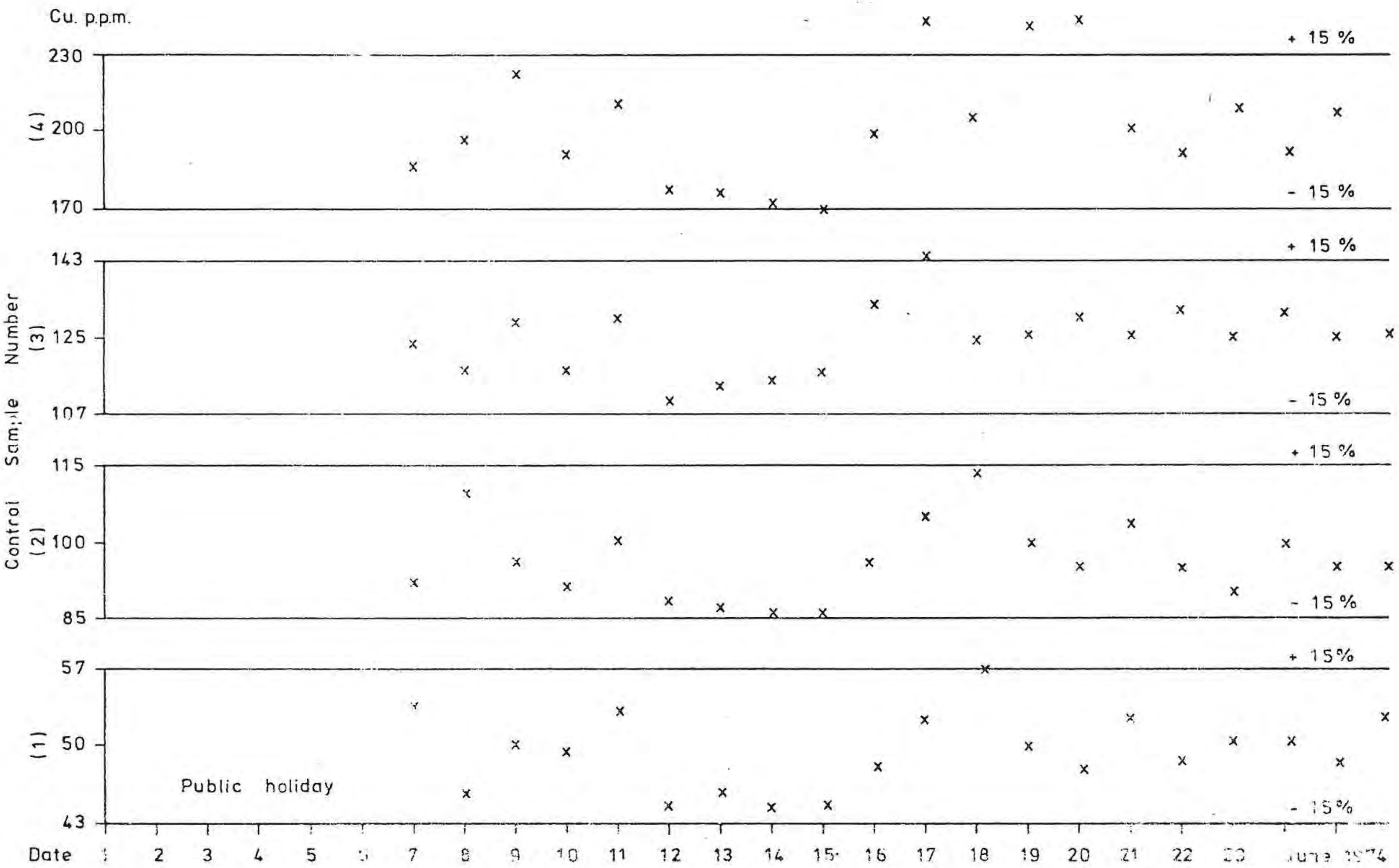

Fig. 2. Standard Control Samples : Copper Hx

In addition, the analytical results of the control samples should be plotted on a control sheet as illustrated by Fig. 2. One control graph is required for each element analysed in each sample. The results are plotted according to time at least twice daily or more frequently.

Plots of the type illustrated in Fig. 2. are normally arranged along the length of a wallboard, whereas those in Fig. 1 could be filed with the duplicate of the analytical results for a particular day and retained in the laboratory.

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