GEOCHEMICAL EXPLORATION IN TROPICAL TERRAINS WITH SPECIAL REFERENCE TO BASE METALS

By

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ABSTRACT

In tropical areas, the high rainfall induces severe and pervasive weathering, producing a thick soil cover. The lithologies underneath may be recognised using geochemical mapping, which is based on certain elements that have the ability to differentiate between various lithologic units. Elements that are independent of the weathering process are normally selected for this purpose.

The chemistry of mobility of base metals is an important factor to take into account when evaluating the mobility and distribution of these elements in a soil profile. Factors such as pH, Eh, organic material, clay minerals, Fe and Mn oxides are normally key aspects to be considered.

When iron-rich rocks undergo deep weathering, lateritic profiles are developed. These are widespread in a belt bordering the equatorial zone, including the Brazilian shield, West and East Africa, parts of India and Northern Australia. In these profiles, the high rainfall promotes intense leaching of the different horizons. Where the pre-existing profiles are mostly preserved, the base metals are distributed throughout the profile: in the upper ferruginous horizon, goethite and hematite can adsorb large amounts of Mo, resulting in large dispersion halo. Other base metals such as Cu and Zn are less resistant in these freely-drained profiles and, therefore, they may be partly leached from the profile. In the lower horizons, Cu, Zn, Ni and Co are retained, hosted in kaolinite and smectite, and thus, a high geochemical contrast will be identified in this horizon at the expense of a decline in the size of the dispersion haloes. The pre-existing profiles can be truncated, with a thin stone line developing at the contact between the lateritic profile and the recent soil. The conditions in these environments favour the retention of most of the pathfinder and target elements in all soil horizons, with the B horizon showing the highest contrast.

If the primary rock is rich in Al, a bauxitic profile will be developed. The world distribution of bauxites closely resembles that of laterites. The behaviour of Co and Ni is very similar to that of iron during the bauxitization. Furthermore, the factors that induce residual enrichment of Al with removal of Fe in the soil profile will cause significant depletion of Co and Ni in these profiles. These metals are then concentrated at the base of the profile because

of precipitation from downward percolating solutions. Many karst bauxite deposits in Southern Europe are enriched with Ni and Co in the basal horizon. Such horizon is mined as nickel ore in the bauxites of the Lokris region in Greece.

Copper and molybdenum are strongly enriched in bauxitic profiles. Concentration ratios are 8 and 3.2 for Cu and Mo respectively. Molybdenum is closely related to goethite and hematite, and therefore, the high concentration of Mo in a bauxitic profile will be consistent with the horizon where iron is concentrated. Copper concentrates at the base of the iron rich-horizon but also appears enriched in the saprolite together with Co.

When sulphide bodies occur, in this environment, deep and penetrative weathering has resulted in considerable near-surface mobilization of iron and silica. The supergene alteration commonly obscures the identity of the primary sulphides at the surface. In this case, geochemical assessment of the resulting gossan has proved to be crucial in mineral exploration. A search in the secondary mineral assemblage, volatile and precious metals may lead to the information on the composition of the primary sulphide assemblage.

The conclusion that will be reached is that if the geochemical properties (mobility, affinities with Fe or Mn oxides and/or clay minerals) of each of the base metals are understood, an appropriate sampling (optimum size-depth combination) will then be done. In such cases, a subdued, weak, but significant, geochemical response will be identified in the surface horizon.

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1. INTRODUCTION

The objectives of this dissertation are to:

i) Describe the geochemical processes taking place in tropical environments.

ii) Examine the chemical processes and the effects they have on the formation of base metal gossans and in the distribution of Ni, Co, Cu, Mo, Pb and Zn in the weathered profiles.

iii) Summarize the dispersion models and the implications for geochemical exploration and evaluation in regard to assessing potential areas of mineralization where a thick soil covers the fresh rock.

In the achievement of the above aims, this work takes a look at some of the literature on the issue of geochemical exploration in tropical terrains, with special reference to base metals.

The extensive mobilization of many elements during intense weathering means that those elements commonly used as pathfinders for base metal mineralizatin cannot be used without a quantitative understanding of their behaviour under conditions of strong chemical weathering. It is significant that prior to 1965 most mineral descoveries in tropical terrains were of weathering resistance, such as gold and tin, or weathering products, such as iron ore and bauxite (Butt and Sheppy, 1974). The increasing use of geochemical exploration techniques has proved to be efficient on identification of base metal mineralization since adequate sampling and interpretative procedures are applied.

It is now understood that while deep weathering commonly has a detereous effect on the strenght of geochemical expression of a mineral deposit, it can also be advantageous. Weaker but larger secondary dispersion anomalies can result in weathered terrain than where a weathered mantle is missing. Where this dispersion is recognised, accurately interpreted and used to advantage, lower cost geochemical exploration is possible.

2. THE TROPICAL ZONES ENVIRONMENT

Tropical zones are typified by high temperatures and high precipitations, two particularly important factors in defining a climatic region. The present climate is of paramount importance in determining the nature of active geochemical dispersion processes in any area. It is the climate of the soil itself that is of most relevant impact on soil processes, but this information is not always available. The atmospheric climate, although a good guide on a regional scale, does not respond to very local factors such as slope, drainage, and porosity.

The principal elements known to have most influence on soil processes are equally temperature and moisture which are derived from geographical distribution of continental blocks and oceans. Temperature determines the rate of chemical reactions during weathering, whilst moisture has a significant impact either as a reagent or as a medium in which reactions take place. Moisture as water acts by transporting the products of several chemical reactions and as a mechanical agent in physical erosion.

The most widely used classification of climates is that of Köppen (1936) in which climate depends on monthly and annual measures for temperature and precipitation. A summary on Köppen climate classification compiled from Strahler (1975) is given in Table 2.1. In this classification the major climatic groups as well as the subgroups and precipitation indicators are given. Table 2.2 provides the world precipitation regions.

Figure 2.1, gives a morphoclimatic world map showing the distribution of the eight climates, (Darnley et al., 1994; based in Budel, 1982). The Köppen classification of climates although useful in general terms, does not always meet the soil boundaries in specific regions. Different climates can produce the same soil type and changes in climate do not always mean changes in soil type (Young, 1976; Trewartha, 1968 in Butt and Zeegers, 1992). Taking into account these considerations, a new classification of the principal climatic zones of the tropics relevant to pedology and vegetation was developed (Young, 1976 in Butt and Zeegers, 1992), Table 2.3.

Table 2.1: The five major climatic groups and respective subgroups (from Strahler, 1975).

The 5 major climatic groups	Subgroups	Annual temperature and precip. indicators
A Tropical climates. Avg. temp. of every month > 18C; no winter season. Annual rainfal > evapor. B Dry climate. Potential evap > ppt. on avg; no water surplus than no streams. C Warm temperate climate. Coldest month avg temp < 18 C, but > -3 C; at least one month has avg temp > 10 C. It has both winter & summer. D Snow climate. Coldest month avg temp < -3C, warmest month avg 10C. E Ice climate. Avg temp of warmest month <10C; no true summer.	S steppe climate: semi-arid climate; 38 to 76 cm of rainful annualy. Applies only to B group. W Desert climate: arid climate. Most regions included < 25 cm/year; applicable only to B group. f Moist. Adequate ppt all months. No dry season; applicable to A, B and C groups. w Dry season in winter s Dry season in summer of the respec. Hemisphere. m Rainforest climate despite short, dry season in monsoon type type of precipitation cycle. Applies only to A climates.	a With hot summer, warmest month over 22C. For C and D climates. b With warm summer, warmest month < 22C , C and D climates. c With cool, short summer, less than 4 months > 10C; C and D climates. d With very cold winter; coldest month < 18C, D climates. h Dry-hot; mean annual tep > 18C. Applies to B. k Dry-cold; mean annual temp < 18C. Applies to B.

Table 2.2: World precipitation regions (from Strahler, 1975).

Name	Latitude range	Contin. location	Ppt/year (Cm)
1. Wet Equatorial Belt.	10 N to 10 S	Interiors, coasts	Over 200
2. Trade wind coasts (Tropical coasts)	5-30 N and S	Narrow coastal zones	Over 150
3. Tropical deserts.	10-35 N-S	Interior, west coasts	Under 25
4. Middle latitude deserts.	30-50 N and S	Interiors	10-50
5. Humid subtropical regions	25-45 N and S	Interiors, coasts	100-150
6. Middle-latitude west coasts	35-65 N and S	West coasts	Over 100
7. Arctic and polar deserts	60-90 N-S	Interiors, coasts	Under 30

Table 2.3: Climatic regions of pedogenic significance in the tropics and subtropics (from Butt and Zeegers, 1992 after Young, 1976).

Climatic region	Mean annual rainfall (mm)	Dry season months <60mm rain	Koppen equivalent	Natural vegetation	Zonal soils
Rainforest	>1800	0-2	Af; Am	Lowland tropical rainforest	Leached ferrallitic soils; Kaolinitic-gibbsitic; always moist.
Rainforest-savanna transition	1200-1800	2-6	Am	Semi-deciduous forest or forest-savanna mosaic and Asian monsoon forest;	Ferrisolic soils on intermediate-basic rocks, less leached than rain-forest; top metre may dry out in dry season.
Moist savanna; two wet seasons	900-1200	3-5	Aw	Forest and grasslands	Ferrisolic soils on intermediate and basic rocks. Moderately weathered and leached
Moist savanna	900-1200	3-5	Aw, Cwa	Forest and grasslands	Ferruginous and ferrallitic soils, pH 5-6;kaolinitic some smectite. Base saturation 40-60%. Leached in wet season, dry to 1 m in dry season.
Dry savanna	600-900	6-8	Aw,Cwa	Grasslands with 5-50% tree cover	Ferruginous and ferrallitic soils, pH 6-7. Base saturation 60-90%. Less intense leaching. Dry to 2m in dry season.
Semiarid (semi-deserts, steppes)	250-600	8-10	BSh	Xerophytic trees, perennial grasses.	Brown calcimorphic soils, sierozems, arenosols and lithosols. Carbonate accumulating in profile. Dry most of year.
Arid (deserts)	<250	10-12	BWh	Bare ground commonly 50%. Xerophytic shrubs, often thorny.	Grey and red desert soils on alluvium. Lithosols, detritus on slopes. Dry most of year.
Tropical, high altitude (>1600m)	>600	0-6	Cwb, Cwa	Evergreen forest, merging to grasslands and alpine at high altitudes	Humic latosols; podzolic at high altitudes.
Subtropical humid	>900	0-3	Cfa	Deciduous woodlands	Leached ferruginous soils
Mediterranean	400-800	2-3	Csa	Mixed forests	Red and brown earths; lateritic podzolics; terra rossa.

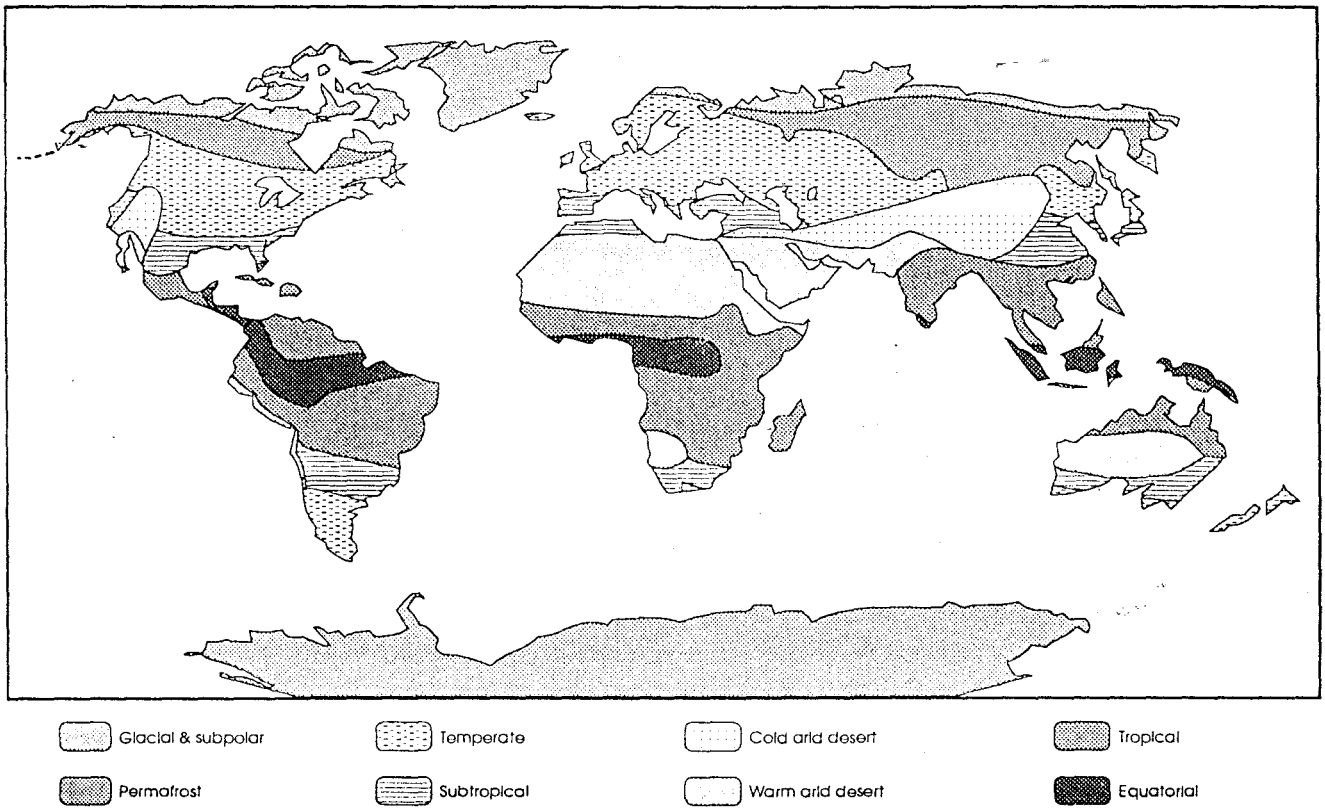

Fig. 2.1: Morphoclimatic world map showing the distribution of the eight climates, (from Darnley et al., 1994; based in Budel, 1982).

3. THE CHEMISTRY OF BASE METALS MOBILITY

3.1. INTRODUCTION

The secondary weathering environment is of fundamental importance to exploration geochemists. Ore-forming metals released during the weathering of primary minerals move away from their origins by means of hydromorphic dispersion or mechanical transport in the area surrounding the source, stream channels, and with the water seeping through the soil profiles. The mobility and behaviour of chemical elements in this environment are determined by, among other factors, the chemical dynamics of reactions and interactions between the metals and water; they are determined by the solubility of these elements in water. The factors which control the solubility are mainly ionic potential, pH, Eh, organic matter and Fe, Mn oxides.

3.2. IONIC POTENTIAL

As established by Goldschmidt (1937), the ionic potential of an element is a number obtained by dividing the ionic charge (Z) by the ionic radius (r). Although this is not a physical or chemical entity, it is a useful concept for helping to determine the mobility of elements. Examining figure 3.1, it can be seen that chemical elements in this diagram are divided into three groups, namely:

(i) Elements with Z/r of less than 3.0 where there are cations like K^+, Na^+, Sr^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} which are soluble and hence mobile.

(ii) Cations with Z/r of 3.0 to 12.0 such as Sc^{3+}, Fe^{3+} Al^{3+}, Zr^{4+}, Mn^{+4} which are not soluble. They tend to be immobile and are precipitated as hydrolysates. They are usually concentrated in weathering residues. It should be understood that while Fe^{2+} and Mn^{2+} are soluble, Fe^{3+} and Mn^{3+} are not soluble and form hydrolysates.

(iii) Elements with Z/r of more than 12 like C, P, N, S, form soluble anionic complexes, becoming more mobile.

It should, however, be pointed out that this is a simplistic approach which does not take into account environmental factors like pH, Eh as well as adsorption. There are elements which are considered immobile in Fig. 3.1 but under certain pH and Eh conditions become mobile such as the case of Mo which can form soluble complexes becoming highly mobile.

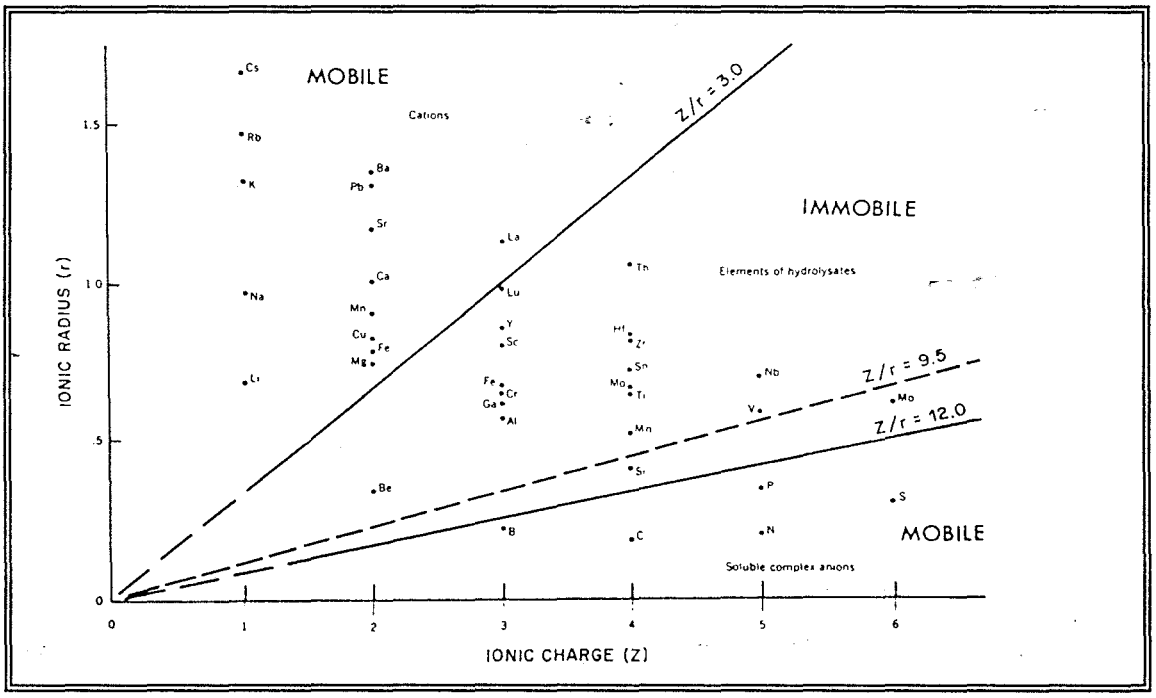

Fig. 3.1: Mobility of chemical elements as function of ionic potential (Z/r). After Levinson, (1980).

3.3. HYDROGEN ION CONCENTRATION (pH)

Hydrogen ion concentration is a numerical expression of how acidic or basic an aqueous system is. Its negative logarithm is known as the hydrogen exponent or pH value. The solubility and thus the mobility of many cations and their compounds is deeply influenced by the pH. The Table 3.1, summarized from Rösler and Lange (1972), gives the pH values for the precipitation of the common cationic hydroxides.

The figures given in Table 3.1 are not fixed; they are a function of the concentration of each cation and the geochemical context where the element is involved. In sulphide deposits, this depends on the interaction between weathering of minerals in the deposit and the weathering of the country rock. The solubility of Cu, Pb and Zn and the potential geochemical mobility of such metals as a function of pH are shown in Fig. 3.2 (Mann, 1982). This graph suggests that pH is a vitally important factor to be considered when assessing geochemical mobility of Cu, Pb and Zn. It also shows that lead is not universally less mobile than copper; it is in the range between pH 2 and 6.2 (normal conditions in tropical environments). But if the pH increases, the relative mobility changes.

Table 3.1: Beginning of the hydroxide precipitation of some base metals as a function of the pH values (compared with those of Mn^{2+} and Fe^{2+}; after Rösler and Lange, 1972).

Ion	pH	Ion	pH
Cu^{2+}	< 5.4	Co^{2+}	< 6.8
Zn^{2+}	5.2-6	Mn^{2+}	8- 8.8
Pb^{2+}	6	Fe^{2+}	5.1-5.5
Ni^{2+}	< 6.7		

The precipitation of these elements gives rise to the formation of secondary minerals. The stability fields of such minerals produced from a variety of solutions can be superimposed to produce a mineral assemblage (Fig. 3.3). This diagram shows the expected secondary mineral assemblages for any given set of solution characteristics, including solution without chloride or sulphate ions and containing carbonate or other solutions (Fig. 3.3).

The carbonate assemblages like malachite, cerussite and/or smithsonite are only stable in neutral or alkaline environments. Azurite replaces malachite as the stable Cu mineral when Pco_2 is more than $10^{-0.4}$. This condition might occur if acid solutions containing copper come into contact with higher pH carbonate solutions associated with weathering wallrock (Mann, 1982). The above results suggest that there will be a wide variation in mobility of these three metals and the equilibria minerals will also be variable. In tropical zones with high rainfall and less prevalent carbonates, the common minerals will be hydrated sulphates (antlerite) and

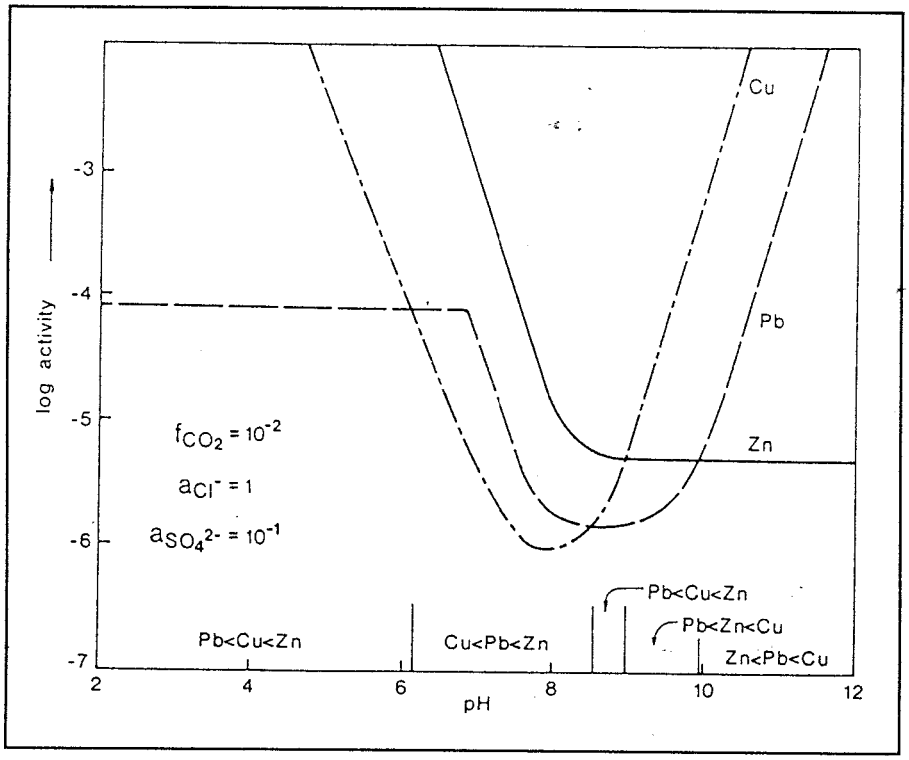

Fig. 3.2: Solubility curves for Cu, Pb and Zn as a function of pH (from Mann, 1982).

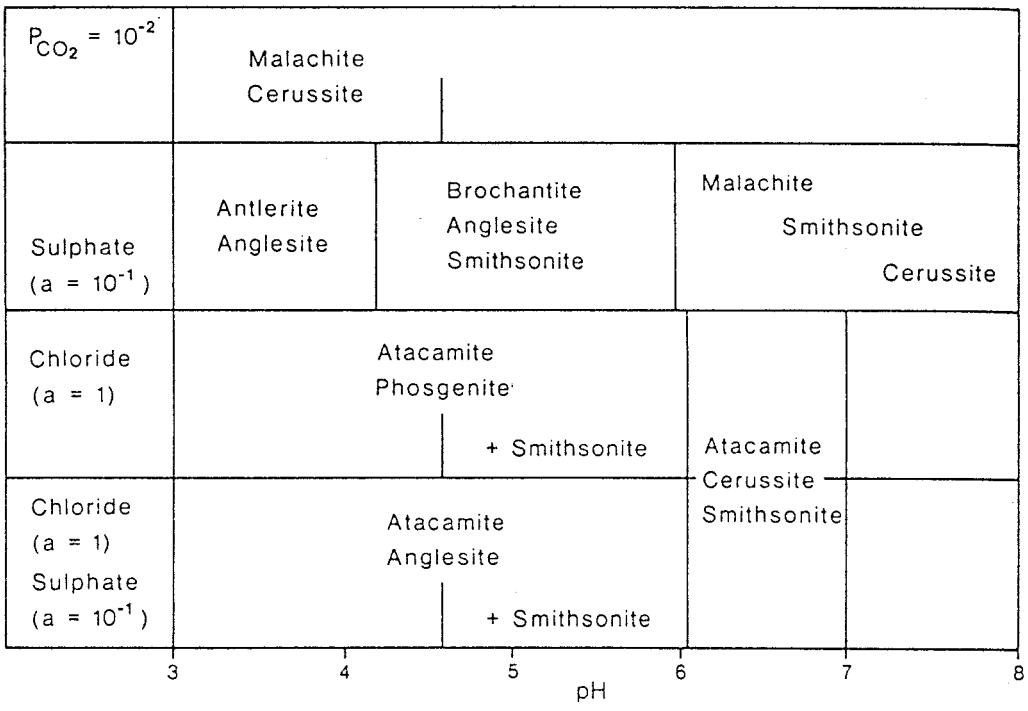

Fig. 3.3: Expected mineral assemblages for secondary minerals of Cu, Pb, and Zn for various solution conditions (from Mann, 1982).

chlorides (atacamite); the last mineral is highly soluble and thus, less stable in freely drained terrain.

The behaviour of copper, lead and zinc can be extended to other cations which also show a U-shape solubility curve in respect to pH (Fig. 3.4). These curves suggest that the cations are more mobile at low pH, reducing their mobility with the increase of the alkalinity; anions, although not represented, are more mobile at high pH. According to Thornber (1992), when the insoluble elements do dissolve, they form cations in acidic and anions in alkalic medium. As a consequence the U-shaped curves shift to give the effect seen in Fig. 3.4. For these curves the minimum is at:

a. High pH values for the cations that have low charge and large size (Fig.3.4).

b. Mid-pH values for more oxidized and positively charged elements with smaller size ions.

c. Low pH values for those elements with a high oxidation state that form Oxy-anions when hydrolysed.

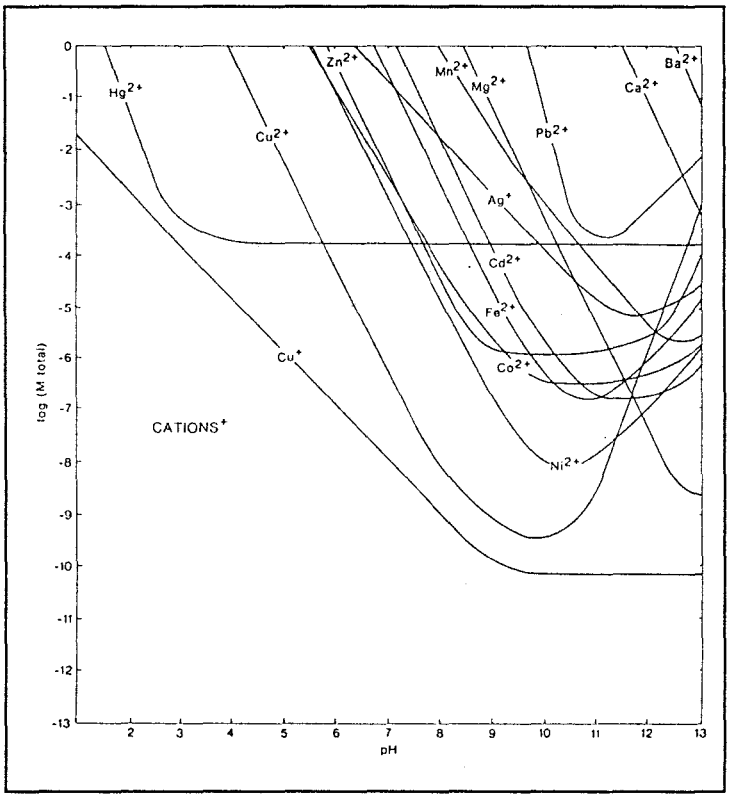

Fig. 3.4: Solubility of various cations and oxides by hydrolysis as a function of pH. (From Thornber, 1992).

3.4. REDOX POTENTIAL (Eh)

Some elements occur in more than one valence state such as the case of Fe as Fe^{2+} and Fe^{3+}; Mn as Mn^{2+} Mn^{3+} and Mn^{4+}; Mo occurs with six valence states; lead in a highly oxidizing environment can pass from Pb^{2+} to Pb^{3+} and copper can be found as Cu, Cu^{1+} and Cu^{2+}. Oxidation could be explained in terms of increase of positive valence or decrease of negative valence, through the loss of electrons at the oxidizing environment. Reduction is understood as decrease in positive valence due to the entrance of electrons.

Taking into account that the process involved is electrical, the oxidizability of any element is expressed in terms of volts, measured against the standard hydrogen half-cell whose oxidation potential under standard conditions is taken as 0.00 volts. The oxidation potential or reduction potential, or conventionally the redox potential, may have values on either side of 0.00. A negative value of Eh means that it is reducing relative to the standard hydrogen half cell.

The pH and Eh values are of extreme importance in understanding the behaviour of various elements in the secondary environment. As stated above, the solubility and hence the mobility of some elements is critically dependent upon their valence state; the example of iron is again useful to illustrate that Fe^{2+} is soluble in acid pH conditions; at pH 5.5, Fe^{2+} begins to precipitate as ferrous hydroxide. Oxidation of Fe^{2+} to Fe^{3+} and its precipitation as ferric hydroxide takes place more rapidly in alkaline environment and at lower Eh. This fact explains the preponderance of ferric compounds in a wide variety of environments. A similar phenomenon occurs with Zn^{2+}; this cation does not change the valence as the Eh varies, so it is stable and soluble in a very large pH- Eh field; as a consequence it is a very mobile element. In sulphides it can be seen that the sulphides of Pb and Zn are more readily oxidised than those of Cu and Mo. Chemical gradients caused by oxidation promote diffusion to occur. Vertical movement of soluble cations cause enrichments of elements such as Co, Ni, Cu, Zn, Mo, Pb and others below the water-table, where secondary minerals are precipitated.

3.5. MOBILITY OF THE SELECTED BASE METALS

During weathering of primary rock, chemical elements are released; some of them can be transported far away from the source but others can be fixed nearby. The mobility of each element is a function of its response to specific pH and Eh conditions. The following is the behaviour of selected base metals when released from any source.

Nickel stability during supergene alteration was studied by Thornber (1975a,b); based in a nickel massive sulphide in Kambalda. The oxidation of Ni primary minerals such as pentlandite ($Ni_5Fe_4S_8$) , millerite (NiS) and heazlewoodite (Ni_3S_2) is responsible for the Ni release. Ionic transport occurs through the groundwater to the anodic region which can be 200 m deep in these tropically weathered soils. The Eh-pH diagram for nickel species is shown in Fig. 3.5, where a large field of millerite stability occurs below the sulphides-sulphate boundary. Ni^{2+}, as from this figure, is notably a very mobile cation under near neutral to acidic conditions. The reaction (3.1) below shows violarite-polydimite being anodically leached to give Ni-Fe cations plus sulphate solution.

$$(Ni,Fe)_3S_4 + 16H_2O \rightarrow 3(Ni,Fe)^{2+} + 4SO_4^{2-} + 32H^+ + 30e^- \qquad (3.1)$$

(Violarite-polydymite)

Nickel in solution can move downwards to the enrichment zone where is fixed in the form of enriched violarite or polydymite, or even as enriched carbonates, as depicted in the equation (3.2) . At the enrichment zone, violarite behaves very much like an ion exchange medium with the nickel, copper and cobalt released from the oxidation reactions above, replacing iron in the violarite (Thornber, 1975a). This leads to incorporation of Co and Cu in the structure of violarite or can lead to the formation of polydymite (Ni_3S_4) which is a highly enriched Ni mineral.

$$(Ca,Mg,Fe,Ni,Cu,Co)^{2+} + OH^- + HCO_3^- \rightarrow (Ca,Mg,Fe,Ni,Co,Cu)CO_3 + H_2O \qquad (3.2)$$

(siderite, gaspeite, huntite, reevesite, malachite,etc).

Nickel can be also swept out from the system since it is soluble under these conditions and some Ni-bearing solution can be incorporated into underground water ; iron will be deposited mostly as goethite.

Cobalt resembles Ni in many of its properties and it always appears replacing Ni in the secondary environment (Fleischer, 1971 in Weatherphol, 1978); equation (3.2) above shows that this element could also appear in the structure of carbonates replacing iron and magnesium. If cobalt is abundant then it can produce proper minerals such as bieberite ($CoSO_47H_2O$) and cobaltomenite ($CoSeO_32H_2O$).

The Eh-pH diagram for molybdenum species is shown in Fig. 3.6. The most important Mo mineral is molybdenite (MoS_2) which occupies the sulphide stable field in the diagram, and a set of aqueous species appears at all the ranges of pH; According to Ney et al. (1976) molybdenite is soluble only under highly acidic and oxidizing conditions, from here, molybdic acid (H_2MoO) may form; from this compound, other different species may form.

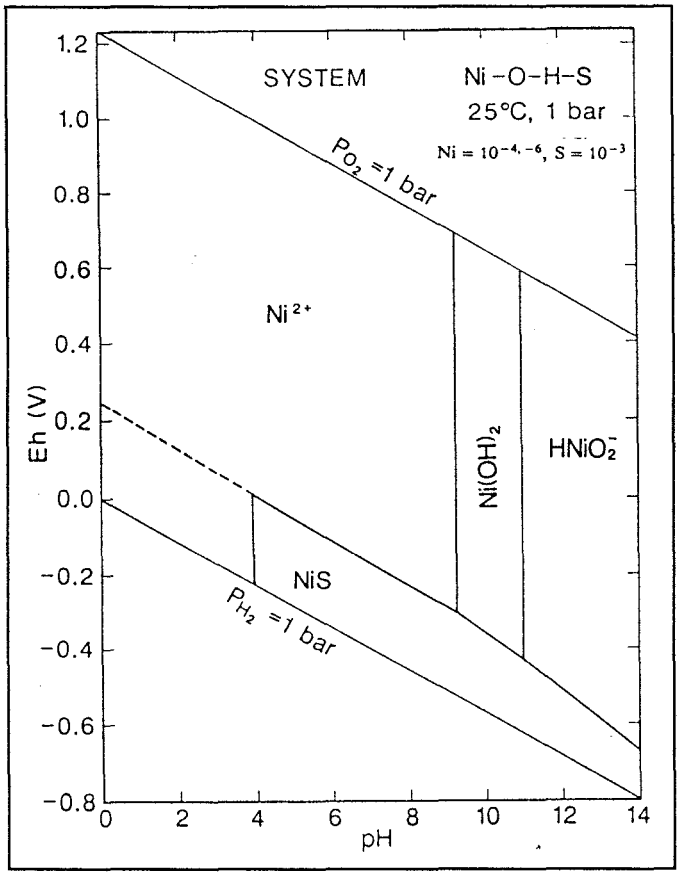

Fig. 3.5: Eh-pH diagram showing the stability field of nickel species (from Brookins, 1988)

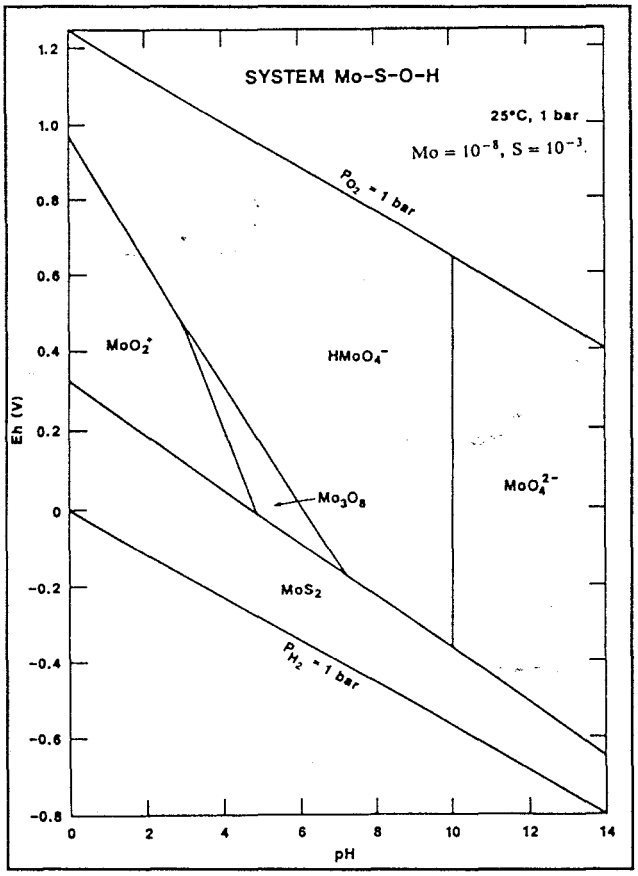

Fig. 3.6: Eh-pH diagram showning the stability field of molybdenum species (from Brookins, 1988)

In the presence of Fe^{3+} in acid water, insoluble ferrimolybdite ($Fe_2O_3MoO_3.8H_2O$) will be formed and precipitation will occur. In neutral water, in the presence of Ca^{2+}, powellite ($CaMoO_4$) may form and at pH higher than 9 powellite becomes extremely mobile (Bloom, 1966). The pentavalent and hexavalent oxidation states are the most common in the normal oxidation processes; they are extremely important species as they render high mobility to Mo

because they form complexes. In fact, in the secondary environment Mo is one of the most mobile elements because of the solubility of its oxygenated complexes with valence +6. During the sulphides oxidation, Mo is present as Mo(V,VI) oxyions which are aqueous species. The precipitation of Mo could occur as MoS_2 in reducing environments.

The mobility of zinc is exclusively dependent on pH, since there is no valence change in this metal. From the weathering of Zn-bearing sulphides, Zn^{2+} is released and new minerals are formed. The stability field of the several secondary zinc species is displayed in Fig. 4.1, which suggests that hemimorphite is the only stable mineral. Zn^{2+} cations are stable at a wide range of pH and remain in solution (Fig. 3.7). If the environment is rich in sulphates, then an aqueous $ZnSO_4$ will be formed and will enhance the mobility of zinc (Southwood, 1986). Under low activity of aqueous silicon in groundwater, hemimorphite does not form, and Zn^{2+} becomes the only stable zinc specie; this fact may explain the broad dispersion halo normally associated with zinc. This behaviour contrasts with that of lead. Lead as a cation is only stable at a very narrow range of pH (Fig. 3.8). Increasing this parameter, secondary minerals form and precipitate mostly as anglesite and some times cerussite. Less common minerals such as planttnerite (PbO_2), minium (Pb_3O_4) and massicot (PbO) can also form as the pH increases. The lower mobility of lead is understood as the result of the instability of either Pb^{2+} or Pb^{3+} at the normal pH, Eh conditions.

In the case of copper, Cu^{2+} cations are often released from the weathering of chalcopyrite, idaite or bornite, as in the equation below:

$$Cu_3FeS_4 + 32H_2O \rightarrow 64e^- + 3Cu^{2+} + Fe^{2+} + 4SO_4^{2-} + 64H^+ \qquad (3.3)$$

(Idaita)

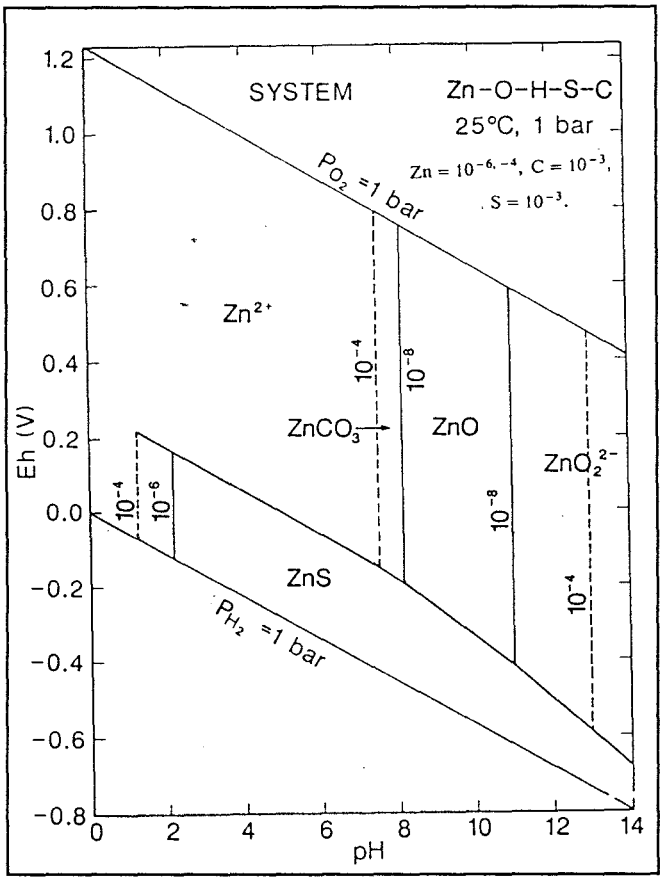

Fig. 3.7: Eh-pH diagram showing the stability of zinc species (from Brookins, 1988).

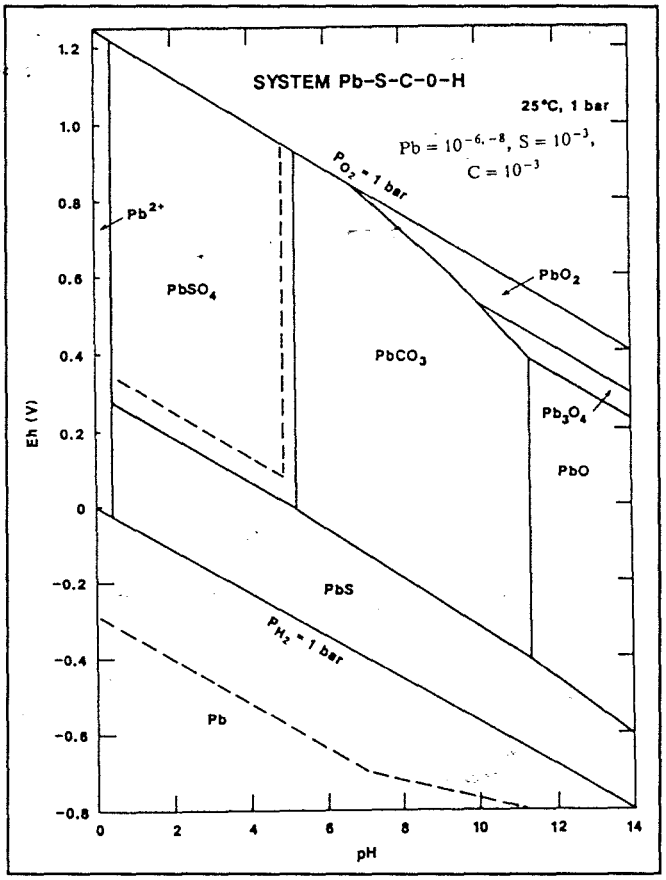

Fig. 3.8: Eh-pH diagram showing the stability field field of lead species (from Brookins, 1988).

Under the prevailing pH, Eh conditions, much of the copper released is soluble in water (Fig. 3.9) and thus, percolates in solution until secondary copper minerals are formed and then copper is incorporated. These minerals are actually the result of the reaction between aqueous copper and chalcopyrite and/or bornite in the enrichment zone. Studies carried out by Titley (1978) have showed that copper is soluble under oxidizing conditions, in such a way that water content measurement along a profile suggested that dissolved Cu^{2+} increases downwards until secondary sulphides are precipitated. The solution composition in copper below the zone of enrichment is very similar to that entering the profile; this suggests that very low copper is swept out from the system. The precipitation of Cu^{2+} as chalcocite (Cu_2O) or covellite (CuS) is controlled by Eh because it occurs when pH is still favourable for Cu^{2+}.

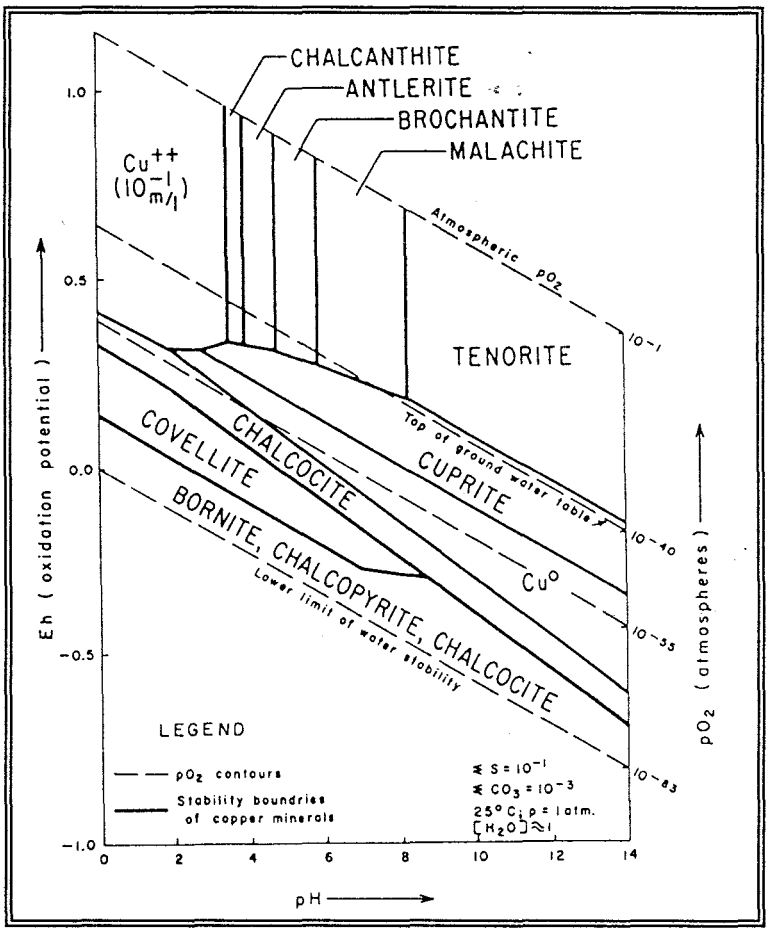

Fig. 3.9: Eh-pH diagram showing the stability field of copper minerals in the system Cu-S-H_2O (from Anderson, 1966).

3.6. ROLE OF IRON AND MANGANESE OXIDES.

The ability of iron and manganese oxides in sediments and soils to scavenge heavy metals in the secondary weathering environment has attracted attention in recent years (Hawkes and Webb, 1962; Chao and Theobald, 1976; Nowlan, 1976; Levinson, 1980; Butt and Zeegers, 1992). The ubiquitous occurrence and chemical reactivity of these oxides make them an important means of transport and deposition of trace elements, determining in this way their mobility. Fe oxides are present in soils as hamatite (Fe_2O_3), goethite (FeOOH), lepidocrosite (alpha FeOOH), magnetite (Fe_3O_4) and hydrated amorphous ferric hydroxide ($Fe(OH)_3.nH_2O$) (Tchao and Theobald, 1976). The amorphous iron oxides are more reactive chemically than the crystalline Fe oxides. Average soil contains more Fe oxides than Mn oxides, but the Mn

oxides exhibit greater chemical reactivity and more complex mineralogy than do the Fe oxides. The chemical reactivity of Mn oxides is related to some specific features of Mn:

(a) Mn can exist in several oxidation states, as stated above. Consequently, it forms nonstoichiometric oxides with variable valence states.

(b) The Mn oxides form co-precipitates and solid solutions with iron oxides (Tchao and Theobald, 1976).

The Fe and Mn oxides are present in stream sediments and soils as coatings, stains and concretions or as discrete particles of colloidal dimensions; they are strong scavengers for many heavy metals released in the weathering processes. The scavenging action is a manifestation of the solid-liquid interfacial phenomenon related to the mineralogical structure and physical/chemical properties of these oxides. This ability of Fe and Mn oxides to scavenge and reconcentrate trace elements from the surrounding environment has been discussed by Nowlan (1976); Tchao and Theobald (1976) as well as by Levinson (1980). The mechanism of scavenges has been summarized as being an electric process (Prof J. Moore oral comm. 1995), and can take place as adsorption, surface complex formation, cation exchange and penetration of the crystal lattice. A quantitative measure of the adsorptive capacity of these oxides was summarized by Hawkes and Webb (1962) referring to marine sediments and showing their high capability in metal adsorption. In a similar manner, limonite from sulphides and hydrous oxide precipitates of iron and manganese in surface drainage channels and soils tends to become preferentially enriched in respect of many minor elements. This work (Table 3.2) strongly suggests that these oxides concentrate base metals. In a subsequent study on the adsorption of trace elements by Mn and Fe oxides, Nowlan (1976) presented a classification of trace elements, as given in Table 3.3.

By adsorbing metals the Fe-Mn oxides determine the behaviour of such elements in the secondary environment. Since the elements in these oxides move according to the mobility of the oxides, being precipitated where the oxides are deposited, they dissolve as redox potential increases and reprecipitate as the system becomes oxygenated (Jenne, 1976 in Tchao,1984). This fact has been extremely important in the mobility of base metals widening their dispersion area (Wheatley, 1974).

Table 3.2: Concentration of some minor elements in iron and manganese oxides sediments (from Hawkes and Webb, 1962).

Element	Avg in igneous rock (ppm)	Content in Fe-oxide sediments (ppm)	Content in Mn-oxide sediments (ppm)
As	2	10 - 700	70
Ba	640	90 - 370	1 000 - 7 000
Cu	**70**	**180**	**2 000 - 20 000**
Mo	**1.7**	**not known**	**300 - 3 000**
Ni	**100**	**20 - 2 000**	**1 600 - 2 200**
Se	0.01	0.5 - 5.0	not known

* In bold, the base metals in discussion

Table 3.3: Classification of trace elements according to their adsorptive capability (after Nowlan, 1976) .

Elements not scavenged by oxides	Elements probably not scavenged by oxides	Elements scavenged weakly by oxides	Elements scavenged strongly by Mn	Elements scavenged strongly by Fe
B,	Ag	**Cu**	**Co**	As
Cr	Be	**Mo**	**Ni**	In
Rb	Ga	**Pb**	**Zn**	
Sc	La	Sr	Ba	
Ti	Sb		Cd	
V	Y			
Zr				

* In bold, the base metals in discussion

3.7. THE ROLE OF ORGANIC COMPOUNDS

The strong interaction between decaying organic matter and inorganic ions may cause either enhanced solubility or complete immobility, depending on the molecular size of the humic material (Thornber, 1992). The attraction between the cation and the OH^- bounded organic compound is known as chelation. The best known synthetic chelating agent is ethylene-diamine-tetra-acetic acid (EDTA). The chelation effect of organic acids over the common base metals is given in Table 3.4; the values are expressed as log (const). The greater the constant, the greater the stability of the complex and consequently the solubility of the chelated metal. Chelation of a cation with humic material may have three effects (Thornber, 1992):

(a) It may be rendered more soluble by chelation with a fulvate molecule.
(b) It may chelate with two soluble humates to form a larger molecule which then precipitates.
(c) It could be chelated into an immobile humin.

Table 3.4: Chelation effect and adsorption by goethite over the most common base metals. (compiled from Thornber, 1992).

Base metal (cation)	Adsorption onto Goethite pH above	Chelation by EDTA	organic acids Fulvic
Co^{2+}	6.5	16.4*	4.7*
Ni^{2+}	6.7	18.2	5.3
Cu^{2+}	4.5	18.9	9.5
Zn^{2+}	6.2	16.44	5.2
Pb^{2+}	5	17.88	6-7

* log constant

The deposition of metals occurs as co-precipitation, which may occur under certain conditions where Fe and Mn oxides are precipitated out of solution along with other metals (Tchao and Theobald, 1976). Co-precipitation is the term describing the precipitation of elements from solutions in which they would normally be soluble, as the result of the precipitation of some other, more abundant elements/oxides (Thornber, 1992). In this case co-precipitation could be understood as the precipitation of cations (those indicated in Table 3.4) as a consequence

of the precipitation of Fe and Mn oxides. From the mineral exploration point of view, because of their scavenging nature, Mn-Fe oxides have potential for being valuable sampling media. Sampling for these oxides can be done in coatings scraped from boulders and pebbles. To control the adsorption capability which can lead to false anomalies, Fe-Mn and target elements should be sampled and ratios calculated, because commonly element/Mn, element/Fe ratios enhance the mineralization. Studies of secondary Fe and Mn oxides and their relationships to the geochemistry of base metals (Zn, Co, Ni, Cu and Pb) provide one of the promising strategies for detecting metal anomalies in deeply weathered terrains.

A summary on mobility of elements in the secondary environment considering some of the factors discussed before, is given in Fig. 3.5.

Table 3.5: Mobility of elements in the secondary environment (after Levinson, 1980).

ENVIRONMENTAL CONDITIONS				
RELATIVE MOBILITY	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 Cu, Co, Ni, Hg, Ag, Au As, Cd Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl

4. THE WEATHERING AND RELEASE OF BASE METALS

4.1. INTRODUCTION

Essentially, any mineral and therefore any rock is only stable under those environmental conditions under which it has been formed. Since these conditions change, minerals become unstable, tending to transform into new mineral forms, which would be stable under the new conditions. Drastic change in the physical-chemical conditions normally occurs when minerals and rocks that were formed in deep-seated primary environments, under magmatic or metamorphic processes are, exposed to meteoric conditions. In this case, most primary minerals will decompose, under the influence of these surface agents; this process is commonly called weathering. Weathering, then, can be summarized as the process of rock alteration as the result of the interaction that takes place at the interface between the rocks exposed at the surface, and atmosphere, hydrosphere and biosphere.

4.2. FACTORS INFLUENCING WEATHERING

The main factors influencing weathering are:

(i) Stability of minerals: A number of minerals although formed under magmatic or metamorphic, conditions are known to remain stable under surface conditions while the majority will be decomposed more or less rapidly.

(ii) Permeability of primary rocks and minerals: a rock or mineral parent material that cannot be easily penetrated by the weathering agents is decomposed much more slowly than a similar one offering a large surface for attack to those agents. The more impermeable a mineral or rock, the more resistant to weathering will be such mineral or rock.

(iii) Climate: Taking into account that the presence of water and the temperature are major factors in the chemical weathering, climatic conditions are of paramount importance in the rate and type of weathering, and subsequently, in the weathering products.

(iv) Topography and drainage: These factors are mainly important in the rate of physical weathering, or mechanical destruction of rocks and minerals, preparing them for chemical attack, their transport and also their period of exposure to a certain environment. In addition, the relief and drainage pattern of any area are important factors in the development of a secondary geochemical environment such as a well-developed soil profile.

4.3. TYPES OF WEATHERING

1. The physical weathering is brought about by agents including temperature, water as a mechanical agent and biological factors. It essentially involves the fragmentation and reduction in size of minerals with little or no chemical changes. In tropical areas very little physical weathering occurs, even though its importance still persists, making the rock more susceptible to chemical weathering by increasing the surface exposed to chemical attack.

2. Chemical weathering is by far the most important in tropical areas and involves the chemical decomposition of pre-existing minerals and subsequent formation of new minerals, under the influence of superficial chemical agents such as H_2O, O_2, CO_2 and organic matter.

Chemical weathering is caused mainly by the attack of CO_2-bearing natural waters on fresh rock, by which certain constituents go into solution, whereas others form a relatively insoluble mineral residue (Schuilling et al., 1988).

Weathering is then controlled by the availability of water and by temperature, two fundamental factors that define the climate, namely annual average precipitation and temperature. The water carries the released components in solution until the concentration is high enough to precipitate secondary minerals. Important for weathering is also the geology, specifically the physical and chemical nature of the ores and host rocks; morphology (land forms, drainage) and groundwater movement. According to Trescases (1992), a zone of active weathering is virtually absent where water is unavailable, such as in very high latitudes and in desert belts. The weathered zone is relatively thin and not strongly differentiated in the temperate middle latitudes. However, it becomes very thick and chemically involved in the tropics, with the formation of laterites.

4.4. TYPES OF WEATHERING REACTIONS

Chemical weathering is the interaction between the fresh rock and chemical agents, mainly CO_2-bearing waters. Chemical alteration of the initial rock can be described by the following general relation:

$$\text{Fresh rock} + CO_2 + H_2O \rightarrow \text{Soil} + \text{Groundwater} \qquad (4.1)$$

Minerals may break down in several ways, as a result of various chemical reactions taking place between these primary minerals and interstitial fluids. The products of these reactions are secondary minerals that form the weathering profiles together with the dissolved material that is removed from the environment by the groundwater, forming the secondary dispersion pattern. Several chemical equations can define the breakdown of primary minerals. According to their importance, three reactions will be discussed here:

4.4.1. Dissolution

The most important dissolution processes occur in the sulphide orebodies and comprise the reactions between water and sulphide minerals liberating cations; the dissolution of sulphide minerals result in decreasing pH, developing an adequate geochemical environment for continuous leaching of metals. Examples of the dissolution processes with respect to the base metals concerned, are given below:

$$PbS + 4H_2O \rightarrow Pb^{2+} + SO_4^{2-} + 8H^+ + 8e^- \quad (4.2)$$

(galena)

$$ZnS + 4H_2O \rightarrow Zn^{2+} + SO_4^{2-} + 8H^+ + 8e^- \quad (4.3)$$

(Sphalerite)

$$MoS_2 + 12H_2O \rightarrow MoO_4^{2-} + 2SO_4^{2-} + 24H^+ + 18e^- \quad (4.4)$$

(Molybdenite)

$$CuFeS_2 + 8H_2O \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \quad (4.5)$$

(Calcopyrite)

$$Ni_2FeS_4 + 16H_2O \rightarrow 2Ni^{2+} + Fe^{2+} + 4SO_4^{2-} + 32H^+ + 30e^- \quad (4.6)$$

(Violarite)

Cobalt resembles nickel in many of its properties, although it is the less abundant of the two.

It frequently occurs with nickel as a solid solution in a variety of minerals (Fleischer, 1971 in Weatherphol, 1978); from Thornber (1975b) nickel and cobalt are reported as following a very similar outline with the nickel being about 100 times more concentrated than cobalt. Once again, this would support the concept that nickel and cobalt behave in a similar manner in the alteration and leaching processes. Examples of replacement between these two can be seen in cobaltian (Ni,Co)SbS and Willyamite (Co,Ni)SbS. Reactions such as those described above are responsible for the liberation of Co and subsequent formation of secondary characteristic cobalt minerals such as brieberite ($CoSO_4.7H_2O$) and heterogenite (CoOOH). The dissolution is one of the critical processes in weathering environment of sulphides because it promotes the leaching of metals in the oxide zone of orebodies, providing cations for subsequent enrichment below the water-table.

4.4.2. Redox Reactions

These are the weathering reactions which involve oxidizing and reducing agents. It was mentioned in Chapter 3 that some elements can occur in several oxidation states. Such is the case for iron, molybdenum, lead, copper and sulphur. In the primary environment, the shortage of oxygen is such that the elements can only appear in the lowest state of oxidation. During weathering, atmospheric oxygen is introduced by percolating solutions and oxidation may occur. This is the case when sulphides such as pyrite are altered to form secondary iron minerals with the liberation of sulphuric acid, as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4.7)$$

$$FeS_2 + 8H_2O \rightarrow 16e^- + Fe^{2+} + SO_4^{2-} + 16H^+ \qquad (4.8)$$

$$Fe^{2+} + e^- \rightarrow Fe^{3+} \qquad (4.9)$$

$$Fe^{3+} + 3OH^- \rightarrow FeOOH + H_2O \qquad (4.10)$$

(Goethite + limonite)

Fine-grained goethite mixed with clay constitutes the limonite. Hematite can be produced as a direct result of the weathering of pyrite (Trescases, 1992).

$$FeS_2 + 8H_2O + 15O_2 \rightarrow Fe_2O_3 + 16H^+ + 8SO_4^{2-} \quad (4.11)$$

(Pyrite) (Hematite)

These reactions, which correspond to the simultaneous oxidation of Fe^{2+} and S^{2-}, contribute to strong acidification of the environment surrounding the sulphides zone, keeping the pH low. In fact, iron rich minerals will tend to produce more acid as they oxidize than those of other metals, for instance Ni rich sulphides.

4.4.3. Hydrolysis

Oxidation reactions are quite common in the meteoric transformation of sulphides. The common reaction, particularly for the weathering of silicates, is hydrolysis. In this process, the ionic species H^+ and OH become incorporated into the structure of minerals; more specifically, there is a reaction between water and the ion of a weak acid or a weak base (Levinson, 1980; Rose and Hawkes, 1979). The hydrolysis of silicates produces hydroxyl anions, cations, dissolved silica and, to a certain extent, secondary minerals. In hydrolysis, an Al- or Fe-bearing silicate is typically converted to a clay or Fe-oxide, accompanied by release of cations and incorporation of H^+, as chemically demonstrated below. According to Trescases (1992), the simplest system is that represented by non-aluminous minerals such as forsterite:

$$Mg_2SiO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4OH^- + H_2SiO_4\,(aq) \quad (4.12)$$

(forsterite)

In this case the weathering does not produce any solid product or residue, because it is no more than the dissociation of all the initial matter. As can be seen from equation (4.12), hydrolysis causes dissociation of water molecules, consumption of H^+ ions and production of OH^- ions. This fact causes the pH to rise and the solution to become alkaline. In tropical

environments, the progressive hydrolysis of olivine results in the total leaching of Mg, developing a profile at the base of which there is an accumulation of F^{2+} hydroxides with Ni^{2+} and Si^{4+} filling the cavities previously occupied by Mg^{2+}. When the hydrolysis of all primary silicates is complete, the residual ferruginous material progressively loses the original lithic fabric by compaction, nodule formation and formation of a ferruginous crust in which goethite is replaced by hematite (Trescases, 1992). The development of such profiles from the weathering of iron-rich minerals leads to the formation of lateritic profiles which will be discussed in Chapter 7. When the hydrolysis involves Al-bearing silicates, aluminium will be precipitated in the weathering environment because this element is least soluble in the pH range of hydrolysis and is not readily removed from the weathering profile. Three types of such reactions are possible according to the nature of the residue (Pedro, 1966 in Trescases, 1992).

- Allitization: formation of gibbsitic residue, where the liberated Al precipitates to form gibbsite.

$$CaAl_2Si_2O_8 + 8H_2O \rightarrow Ca^{2+} + 2OH^- + 2Al(OH)_3 + 2H_2SiO_{4(aq)} \qquad (4.13)$$

(Anorthite) (gibbsite)

When Fe is also present, the plasma is both ferruginous and gibbsitic and the reaction is referred to as ferrallitization. This mechanism is an important process in lateritization.

- Monosiallitization: formation of a kaolinitic residue, consisting of a phyllosilicate phase.

$$CaAl_2Si_2O_8 + 3H_2O \rightarrow Ca^{2+} + 2OH^- + Al_2Si_2O_5(OH)_4 \qquad (4.14)$$

(Anorthite) (kaolinite)

The reactions 4.13 and 4.14 differ in that the latter uses less water and thus can occur in less hydrated weathering environments.

- Bisiallitization: formation of a smectite residue. The liberated Al recombines with silica and commonly with iron to form smectite:

$$CaAl_2Si_2O_8 + 1.4SiO_2 + 2H_2O \rightarrow Ca^{2+} + 2OH^- + (Si_{3.7}Al_{0.3})O_{10}(OH)_2Ca_{0.15} \quad (4.15)$$

(Smectite)

The bisiallitization process consumes even less water than reaction 4.14 and takes place in poorly drained environments from which leaching of basic cations is only partial.

In the foregoing cases, where the primary rock is Al-rich, the weathering of such rock under tropical climates can lead to the formation of bauxites which consist primarily of a mixture of aluminum hydroxides including gibbsite, boehmite and, to lesser extent diaspore (Neil and Gian, 1993). A more detailed account of the distribution of base metals in bauxites is given in Chapter 8.

4.5. BIOLOGICAL AGENTS IN WEATHERING

Organic matter (as used in this dissertation) consists of plants, bacteria and organic compounds. The fact that chemical weathering does not take place to any significant extent where biological processes are not active, such as in very cold or very hot deserts is, by itself, an indication of the profound importance of living organisms in chemical weathering. Organic matter can be divided according to its solubility in NaOH (Levinson, 1980). In this context, humins are soluble in NaOH while fulvic acids and humic acids are not. Further, in this classification, it can be seen that fulvic acids are soluble in acids and humic acids are insoluble.

The real role of such matter is diversified; deep-rooted trees are capable of removing significant amounts of dissolved metals (through base exchange around rootlets) from depths of as much as 40 metres to the surface. The humic and fulvic acids are capable of removing metal cations by the process of chelation- the humic acids have adjacent carboxylic acid and OH groups, that allow the formation of chelation bound with metals ions. They are capable of adsorbing and accumulating metals to anomalous levels.

Micro-organisms are capable of promoting and catalysing the oxidation and dissolution reactions for sulphides. The most important agents, Thiobacillus ferrooxidans bacteria, can oxidize ferrous iron, and Thiobacillus thiooxidans can oxidize sulphides to sulphates. The Thiobacillus ferrooxidans bacteria, which are found in acid mine waters (pH of 2-3) can oxidise both Fe and S compounds, enhancing the production of H_2SO_4, and thereby bring about the release of Zn and Mo from sphalerite and molybdenite respectively (Levinson, 1980;

Eckhardt, 1985). Base metal minerals (bornite, chalcopyrite, galena, sphalerite, millerite, cobalt sulfide and molybdenite) can be directly biograded by these micro-organisms; the metal leaching is accelerated considerably more by applying Thiobacillus ferrooxidans in comparison with the chemical (sulphuric acid) leaching technique (Eckhardt, 1985). Another crucial role played by organic compounds is the determination of the mobility of chemical elements in the secondary environment and soil profiles. Humic acids can dissolve, complex and transport metals either in the soil profile or even in superficial dispersion (Bowell and Foster, 1993).

4.6. RESISTANCE OF MINERALS TO WEATHERING

The resistance of minerals against weathering by meteoric solutions depends mainly on their crystal structure, their composition, the composition of the weathering solution and on the rate of percolation of such solutions. Under normal weathering conditions Mg- and Ca-bearing minerals such as olivine, anorthite rich plagioclase, pyroxene and carbonates are the least resistant to chemical weathering. These are followed in the sequence of resistance, by sodium silicates like albite, and Fe-Mg-bearing micas, including biotite. Quartz, k-feldspars and muscovite are among the most resistant minerals. Only a few minerals are stable under weathering conditions; these are often characterized by poor crystallinity or even amorphous, and most are hydrated minerals. Table 4.1 gives the relative chemical stability of primary minerals under weathering conditions.

The local factors, such as mean annual temperature and degree of leaching, determine, to a large extent, the nature of weathering products. They determine whether montmorillonite, kaolinite or laterite profile will form. However, the nature of the parent material is also important.

4.7. PRODUCTS OF WEATHERING

The direct weathering product is soil which can contain the products of weathering of both rocks and ores. These products can be grouped into three categories (Rose et al., 1979; Levinson, 1980; Joyce, 1984): residual primary minerals, insoluble secondary minerals formed under weathering conditions and soluble constituents.

Table 4.1: Relative chemical stability of minerals during weathering process (after William, 1978).

	Very stable	Stable	Fairly stable	Unstable
Rock-forming Minerals and Accessories	Quartz corundum spinel topaz Tourmaline zircon	K-feldspar Na-feldspar muscovite andalusite garnet kyanite sillimanite	actinolite apatite chloritoids diopside epidote staurolite	amphiboles biotite Ca-plagioc. calcite chlorite dolomite feldspathoids glauconite gypsum olivine pyroxenes
Ore and Economic Minerals	chromite diamond gold platinum rutile	barite cassiterite **galena** ilmenite magnetite monazite niobio- tantalite thorianite	hematite scheelite wolframite titanite	arsenopyrite **chalcopyrite** fluorite **molybdenite** **pentlandite** pyrite **pyrrhotite** **sphalerite**

* in bold, the source of the base metals in discussion

4.7.1. Residual Primary Minerals

Although all minerals formed under primary, deep-seated, conditions are essentially unstable in the surface environment, decomposition by weathering proceeds so slowly with certain minerals that they may be considered as stable, becoming residual minerals (Borsch, 1985). If their resistance coincides with high specific gravity, they can become concentrated to form placer occurrences. This may be the case for minerals including Au, diamond, Pt, cassiterite, columbite-tantalite, chromite and beryl among others. It is relevant to bear in mind

that minerals that are reasonably resistant chemically may yet be too friable or soft to withstand physical weathering. This is the case for wolframite, scheelite, and barite which tend to be resistant to chemical weathering but quickly pulverized by abrasion during erosion and transport. Residual minerals are normally mechanically transported. Mechanical dispersion tends to produce high contrast patterns of limited dimensions which can be modified by down slopes or diluted by barren material.

4.7.2. Secondary Minerals

On weathering, primary minerals tend to undergo both leaching and hydrolysis forming, as a product, a suite of characteristic secondary minerals. Silicates normally form clay minerals during hydrolysis. These clay fraction minerals are geochemically very active because of their large specific surface, their high ion exchange capacity and their adsorption potential. The relevant secondary minerals derived from silicates are the alunite-garosite family, smectites and kaolinites. The alunite-garosite family present the formula $AB(XO_4)_2(OH)_6$. Their structure is such that from the Goldschmidt replacement lows (Goldschmidt, 1954; Krauskopf, 1967), most of the base metals can be found in the structure of these minerals, provided that, during their formation, such metals are available in the environment; hence, Pb^{2+} will be held in A sites while Cu^{2+} and Zn^{2+} can be encountered fixed in B sites; the replacement process ends up with the sulphides vicinity enriched with new minerals such as beaverite, $Pb(Al,Fe,Cu)_3(SO_4)_2(OH)_6$. The formation of these minerals from the country rock in weathering, allows these base metals to be partially fixed and concentrated near orebodies. Kaolinite and smectite are members of the clay minerals with high cation exchange capacity (3-15 for kaolinite and 80-150 meq/100gr for smectite). The cation exchange capacity is a measure of the clay minerals's capacity to adsorb heavy metals. In soil profile, for instance, these minerals, using the property described above, adsorb and concentrate base metals at specific horizons. These horizons are important in exploration geochemistry because they give the best contrast and, therefore, the best indication of the potential of the rock underneath.

In weathering of sulphide ores, the oxidation reactions become more important and a specific suite of secondary minerals is produced. Unlike clay minerals, many of these are visibly crystalline. Residual hydrous Fe-oxides derived from the oxidation of Fe-bearing

sulphides produce either goethite, hematite or limonite. Goethite is also an important mineral because of its high adsorption capability. Levinson (1980) emphasised that the concentration of metals such as Zn, Cu, Ni and Co in B-Soil horizon is mostly due to iron oxide rather than any other component. Table 3.3, gives the affinity of certain metals with oxides (including Mn oxide). In that table it can be observed that, although Cu, Mo and Pb are weakly adsorbed, Co, Ni and Zn are strongly adsorbed by oxides.

Goethite, limonite and jasper are the main constituents of gossans; these arise most commonly from the weathering of pyrite, marcasite, pentlandite, sphalerite, pyrrhotite, arsenopyrite, siderite, and ankerite. In the base of the equations described in point 4.4.1, is suggested that two main parts are formed from the dissolution of each sulphide mineral: the cation and the sulphate radical. The cation can be transported with the percolating water until the enrichment zone where new minerals are formed; this is the case in the enrichment of bornite with Cu^{2+} resulting in chalcosite, and the violaritization of pyrrhotite by adding Ni^{2+} in Fe^{2+} sites, in the pyrrhotite structure (see Figs. 6.4 and 6.5 for more details).

In the case of Zn^{2+} released from the sphalerite, it can produce secondary minerals dependent only on pH, since there is no valence variation. Under these conditions two main minerals could form, hydrozincite and hemimorphite. Hydrozincite is a scarce mineral in humid regions because of its stability field (Fig. 4.1). This mineral is stable in solutions which are in equilibrium with air ($P_{CO2}= 3 \times 10^{-4}$) with a pH higher than 8.1. The scarcity of such alkaline water in nature explains the rarity of this mineral in tropical environments. Zinc hydroxide is also rare and this could also be understood from the Fig. 4.1. Hemimorphite is the main mineral to be expected in this environment, mostly when the pH is less than 7 (Takahashi, 1960). Another product from the weathering of sphalerite is $ZnSO_4$, which is highly soluble and does not precipitate at all. Under a low activity of aqueous silicon species in groundwater, the aqueous Zn^{2+} ions are the only stable zinc specie.

The stability field of galena, anglesite and cerussite have been calculated (Brookins, 1988; Sato, 1992) in terms of pH and Eh (Fig. 3.8). In humid terrains, in sulphide weathering environments, where the pH should be below 6, then the only possible species after galena are anglesite and pb^{2+} ions, with lead showing a very narrow stability field. This fact supports the low mobility of this base metal as it is stable in a very limited pH range.

Molybdenum occurs in several valence states; thus, it is highly dependent on Eh and pH

conditions. In the zone of oxidation, the common secondary molybdenum minerals are powellite ($CaMoO_4$) and wulfenite ($PbMoO_4$).

From the weathering zone, base metals may also be leached away, provided that they form soluble compounds and are not trapped by precipitation, adsorption, co-precipitation or other method; they, then, form a secondary chemical dispersion halo. The secondary dispersion halo is of crucial importance in geochemical exploration because it increases the area of dispersion of the elements increasing in the same way the likelihood to detect the mineralization.

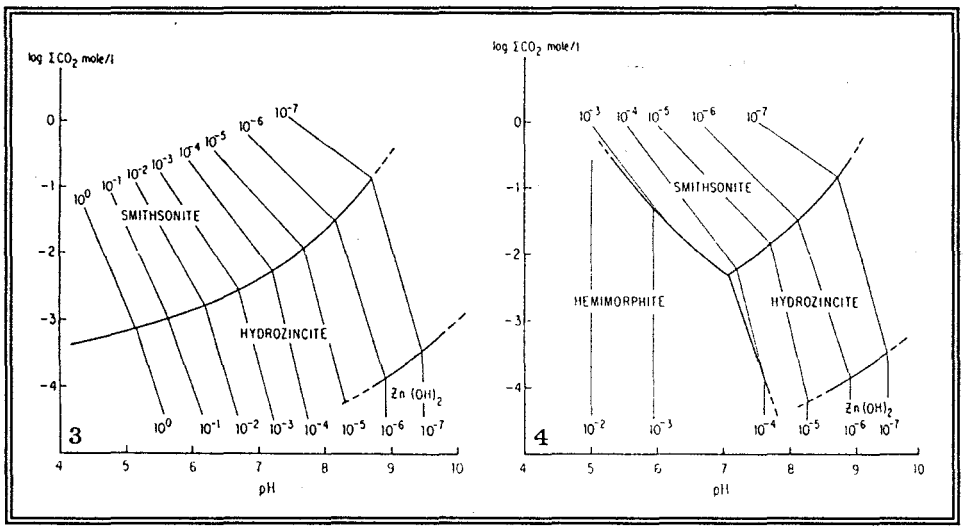

Fig. 4.1: Stability field of zinc species in a solution free of silica (3) and with silica (4) (from Takahishi, 1960).

4.7.3. Soluble Products

During the process of weathering, especially when abundant water is available which is freely drained, certain compounds of primary minerals are dissolved and removed from the system. These soluble products are predominantly elements, ions or complexes which are highly soluble under the weathering conditions. In this context, the solubility of the base metals is a function of the physical-chemical environment (pH and Eh). The diagrams displayed in Figs. 3.2 to 3.9 show in terms of pH and Eh the window where each of the base

metals can be considered stable and soluble either as a divalent cation (Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}), neutral or univalent (Cu, Cu^{1+}) and as oxy-anions ($HmoO_4^-$, MoO_2, MoO_4^{-2}, $HNiO_2^-$).

Molybdenum, because it oxidizes to +5 and +6 oxidation states, shows an increase in solubility and mobility with the Eh due to the formation of oxy-anions. The presence of organic matter can enhance or reduce the solubility of base metals according to the character of the resulting complex. According to Thornber (1992), organic matter has the greatest exchange capacity, ranging from 150-400 meq/100 gr of any of the soil fraction containing humic material.

The stability constants - given in log (const)- of the chelate compounds that EDTA and fulvic acids form with the base metals are listed in Table 3.4. Considering that the greater the constant, the greater the stability of the complex, it becomes clear that EDTA is one of the most important chelation agents for the base metals. This applies for all base metals listed in Table 3.4 but especially for cu^{2+}, Ni^{2+} and Pb^{2+}. Fulvic acids can also, although to a lesser extent, enhance the mobility of base metals, particularly for Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}. Fulvic molecules can also attack stable minerals, leaching and dissolving metals; in this case, they are important in increasing the solubility of the base metals.

In using table 3.4, one should take into account the predominant organic phase in a given soil so as to assess the type and the extent of the chelation effect on metals mobility.

Goethite and hematite are the most common oxides in this environment; physically they change from positively charged to negatively charged as the pH increases. In the same way, more cations become adsorbed from the solution as the pH increases. Table 3.4 gives, for each base metal, the pH from which it starts to be adsorbed onto goethite and thus to precipitate.

Soluble products are normally transported by hydromorphic means. Hydromorphic dispersion tends to give rise to broader, lower amplitude patterns close to mineralization; and can also produce secondary, displaced features similar to or even higher than those identified close to mineralization in seepage, nearby streams or lakes.

The following is a summary of the chemical effects of deep weathering (Butt and Zeegers, 1992).

1. Leaching of mobile constituents:

- Most of the base metals are soluble at specific pH and Eh conditions

2. Formation of stable secondary minerals:
   - alunite-garosite family and clays minerals (kaolinite and smectite).
3. Partial leaching of less mobile constituents:
   - silica, alumina, tintanium.
4. Mobilization and partial reprecipitation of redox-controlled constituents:
   - iron and manganese as oxides
5. Retention and residual concentration of resistant minerals (Table 4.1).

5. SOIL FORMATION IN TROPICAL ENVIRONMENTS

5.1. INTRODUCTION

Considering that in tropical environments the primary rock is seldom available for sampling or detailed studies on the possible mineralization, soil cover becomes one of the principal sample media available for mineral exploration. An understanding of the nature and origin of this soil is essential; it can help in recognising the main constraints it imposes on geochemical exploration and hence in devising suitable and effective exploration techniques applicable in these terrains.

In order to understand the behaviour of chemical elements in this secondary environment, it is crucial to have prior knowledge of the process of soil formation and the characteristics of each of its constituents. Pedogenesis is the result of the chemical transformation of the primary rock due to the instability of the minerals under meteoric conditions. According to Lucas and Chauvel (1992), the nature of this transformation depends on the balance between three main processes: weathering of minerals, transport either in solution or as solids and authigenesis of secondary minerals. The persistence of these factors as the weathering proceeds determines the development of the soil profile.

One of the characteristic features of any soil is the layering evident in vertical sections. These layers differ from each other and from the underlying parent material in their properties and composition. Apart from differences in colour and textures which aid recognition in the field, the properties of greatest significance are those that affect the geochemical dispersion of the elements, such as pH, organic-matter content, clay-mineral type and assemblage, and the amount of Fe-Al-Mn-oxides (Rose et al., 1979; Levinson, 1980).

Profile development is the result of the vertical (upward and downward) movement of material in solution and suspension, accompanied by a complex series of chemical reactions, many of which are organic in origin. Water is the essential medium in which this transfer and reconstitution take place (Rose et al., 1979). The physical-chemical conditions are generally more aggressive towards mineral components in the upper part of a profile because of the presence of biochemical compounds (Lucas and Chavel, 1992). Such compounds facilitate the alteration by the action of water-soluble acids produced either by organisms or from the normal decomposition of organic matter.

This mechanism was previously explained by Levinson (1980), who recognised that the humic part of a soil profile is characterized by a pH of four or less, because of carbonic acid and various organic acids. Although these acids are weak, they move downwards to lower levels where they react with other minerals. As a result, the soluble products released by the weathering processes, as well as some colloids and minerals are continually moved downwards in solution or suspension by circulating waters. It is known that the organic acids and complexing agents generated in humus by bacterial action, and the CO_2 generated by decay of humus, promote the leaching which is a characteristic feature in the A horizon. During this process, minerals and chemical elements are redistributed. Following Rose et al. (1979), the bases (Ca, Na, Mg, K) move downwards as dissolved ions; and Fe and Al move as colloidal particles of clay minerals and oxides, or as complexes with organic groups, or even as free ions or ions complexed with hydroxyl in highly acid soils.

Most of the base metals released from the dissolution reactions (Ni, Co, Cu, Zn, Mo) are soluble and therefore they also move downwards in solution. Resistant primary minerals (Table 4.1) and remnants of primary rock tend to remain behind in the upper soil. The highly leaching processes described above define the A horizon. Commonly, colloidal silicates, oxides and organic matter together with dissolved material are accumulated immediately beneath the A horizon, defining the B horizon. As a result the B horizon is characterized by an enrichment in clay and Fe-Al-oxides, being known as illuviation or accumulation horizon. It is generally brown or orange-brown in colour, harder when dry, often with prismatic textures. These properties are reflexion of the high concentration of iron/or aluminum oxides, usually in combination with manganese oxides and some organic matter.

Because the B horizon is the one of accumulation of elements, either trapped in clay minerals or adsorbed by iron and manganese oxides, this is the horizon sampled in geochemical exploration. However, an orientation survey should be conducted so as to certify that the highest contrast is found in this horizon.

The C horizon consists of more or less weathered parent material and, unless in transported overburden, it grades to the fresh rock which is known as D horizon. This horizon is characterized by the total lack of organic material and the textures resemble the original rock.

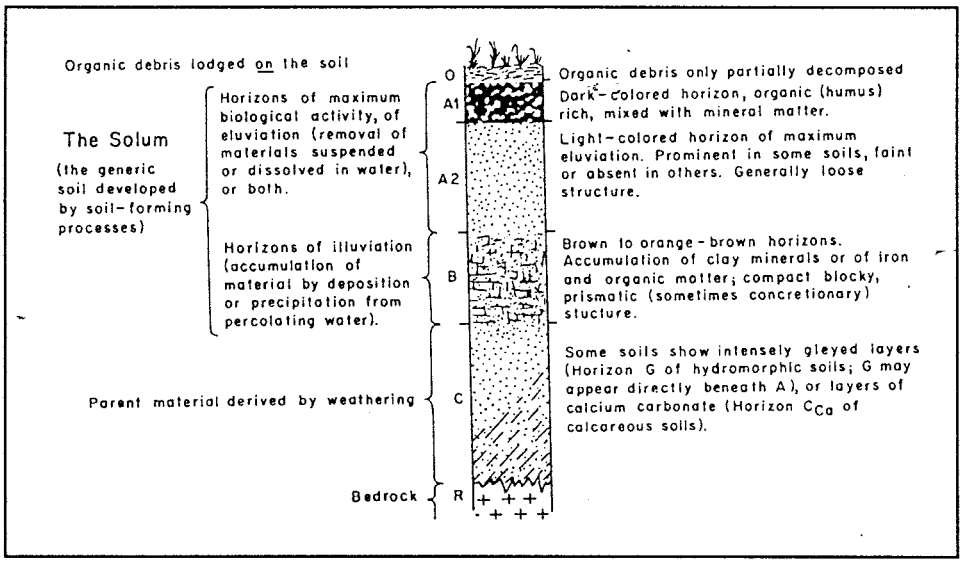

Fig. 5.1: Soil profile as stratified in horizons (Rose et al., 1979).

5.2. SOIL CLASSIFICATION AND DISTRIBUTION

Exploration geochemistry is concerned with classification of soils because there is a need to recognise different types of dispersion during soil formation processes, and there is a need to correlate these dispersion patterns with possible important sources. As seen previously, there are soils with well developed horizons; in this case the trace elements will be found concentrated in specific layers due to the affinity with the mineralogy and/or chemistry of those layers. In other soils with poorly developed layers, specific exploration procedures should be designed in order to meet the specific soil characteristics. This illustrates that for a geochemist, a soil classification should be based on the stand-point of its mode of genesis, geochemical processes operating in the soil profile taking into account environmental factors like temperature and climate. In general, three categories of soil may be distinguished elsewhere in the literature (Rose et al., 1979; Levinson 1980; Borsch, 1985; Butt and Guvett, 1992):

(i) The zonal, also known as climatic classification of soils is based on the premise that climate and vegetation control the nature of the soil.

(ii) Intrazonal soils are those whose formation is influenced not only by climate and vegetation but also by local factors such as nature of parent material, relief and age.

(iii) Azonal soils are those without any distinctive genetic mode; they are deeply influenced by their parent material, rather than by any soil forming process.

In connection with this dissertation, the climatic classification is the most important because all the features are products of geochemical processes which occur only under specific climatic conditions. Aluminium and iron dominate the geochemistry of pedalfer soils (soils with two elements - Fe and Al). They develop in regions with average rainfall of more than 625 mm/yr. Podzols are humid, forest soils common in the northern part of the temperate climates (Fig. 5.2). The abundance of organic matter develops an acid environment (pH about 4), which is responsible for intensive leaching and the subsequent transport of base metals in solution. The leached Al and Fe are carried downwards and deposited as hydrated iron oxides along with clays in the B horizon. The leached nature of the A horizon is shown up as a grey-white colour while the illuviation character of B horizon comes out from the brown colour due to the iron-and-clay hard pan developed. In the humid tropics, the podzolisation process becomes very intense leading to the formation of laterites for which a detailed discussion is given in Chapter 7.

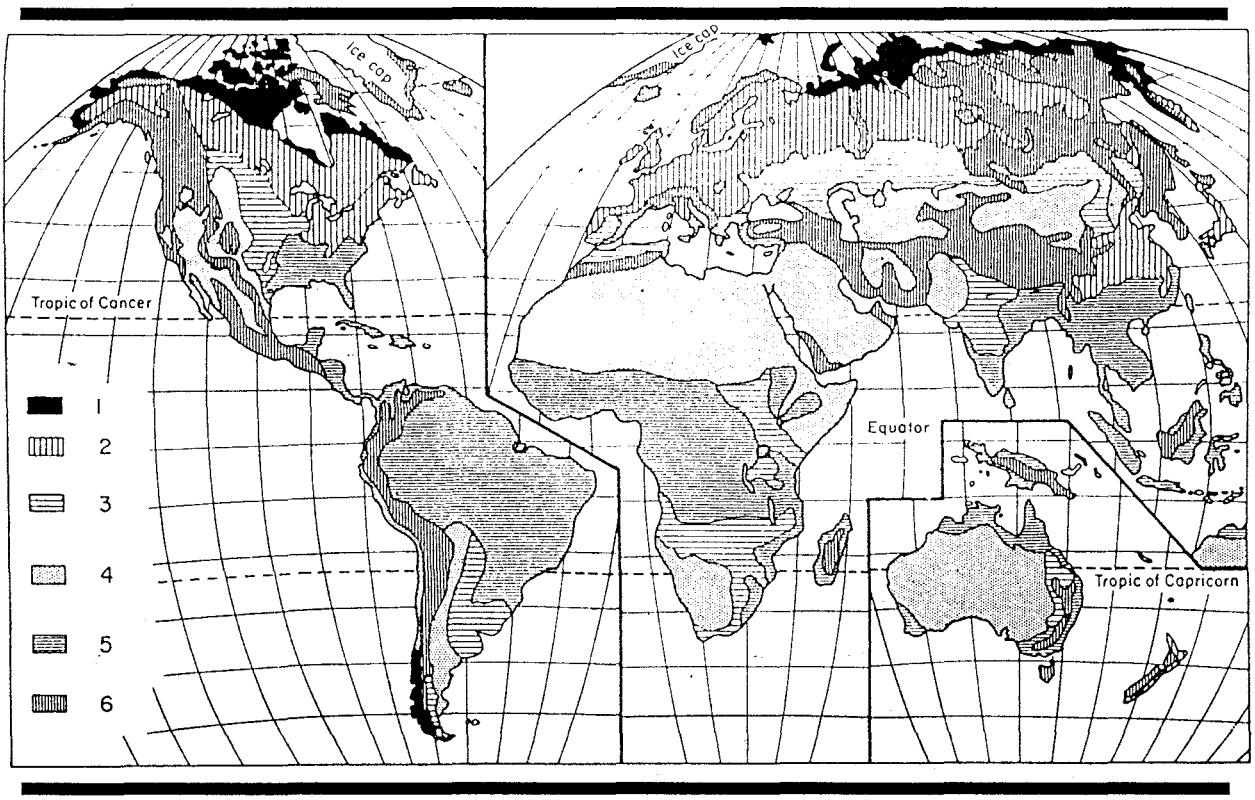

Fig. 5.2: Map of the world, showing six broad soil zones. (1) Arctic soils; (2) Podzolic soils; (3) Grassland soils; (4) Desert soils (5) Tropical soils and (6) Mountain soils. From Rose et al. (1979).

5.3. CHARACTERISTICS OF THE TROPICAL WEATHERED TERRAINS

Tropical regions are characterized by deeply weathered terrains. In these regions, lithosols are common only on steeper slopes in the ranges. Where relief is lower, extensive chemical reworking of the parent material takes place continually; organic matter can accumulate and differentiated profiles, such as in podzols and podzolic soils, may develop (Butt and Smith, 1980). This gives rise to thick and well profiled soil in these environments. In high-rainfall, poorly drained areas, peaty soils are encountered. As a consequence, complex relationships can be developed between the chemistry of residual soils and their parent material which can be the bedrock or a previously weathered rock. In this case, sampling consistently within one soil horizon becomes critical because any variation in metal content can then be related either to bedrock variation or to an important source requiring identification. Laterites and bauxites are special cases in tropical soils.

5.4. BASE METALS IN SOIL PROFILE

Exploration geochemistry in tropical areas is generally addressed to soil cover, since there is a shortage of outcrops. Sampling the particular soil horizon which will yield the highest contrast should be the aim for ore deposit identification. It was previously shown that during the weathering process, chemical elements are released from the primary minerals. Some elements are leached away from the environment but most are mobilized and they integrate into the soil-forming process, being transported and deposited at a certain depth. The distribution of elements in soil profiles is dependent upon two fundamental factors: the abundance of the elements in the parent rock and the nature of the weathering and soil-forming processes operating in these rocks (Levinson, 1980). The forms in which trace elements can be held in soils have been summarized by Mitchell (1972) as including:

(1) in solution in ionic or combined form;
(2) as readily exchangeable ions in inorganic or organic exchange-active complexes;
(3) as more firmly bound ions in the exchange complexes;
(4) in insoluble organic or organo-mineral complexes;
(5) incorporated in Mn and Fe oxides and
(6) in secondary minerals in a fixed form.

The amount of base metals present in any one form depends on the nature and amount of the clay and organic matter as well as the pH and Eh of the soil and the properties of the element under analysis. Thus, the relative importance of the base metals residence sites in soil profile cannot be universally established because of variations produced by local geologic and geochemical conditions. Each of these partitioning sites has been demonstrated to be of maximum importance to the base metals total concentration in the soil (Robinson and Carpenter, 1979).

Iron oxides, grain coatings, chlorite, limonite, chalcedony and kaolinite are the most important residence sites of Cu, Pb and Zn in the anomalous profiles (Robinson and Carpenter, 1979). The residence site for Mo is commonly iron oxide. Table 5.1 below gives the correlation coeficients between trace metals and minerals adsorbing Pb, Cu and Zn (Robinson and Carpenter, 1979).

Table 5.1: Correlation coeficients between base metals and hosting minerals (Robinson and Carpenter, 1979).

Base metal	Hidro-biotite	Biotote	Chlorite	Limonite	Chalcedonia	Kaolinite	Orthoclase
Cu	-.078	-.136	.435	.723	.599	.028	-.161
Pb	.070	-.502	-.151	-.114	-.234	.691	.049
Zn	.011	.090	.172	.423	.375	.088	-.022

In tropical environments, there is intensive leaching and subsequent formation of well layered soil profiles. The B horizon is known as the one where the concentration of clay minerals, manganese and iron oxides is high (Fig. 5.3). The ion exchange capacity of some clay minerals increases with pH. This will enable these minerals to adsorb more cations as the depth increases towards the B horizon because increases the pH of the soil in this direction. These arguments suggest that the concentration of trace elements will be high in the B horizon, taking into account that the elements which appear in soils are basically held in clay minerals, or adsorbed in oxides that collectively accumulate in this horizon. Figure 5.3 shows the variation in metal content with soil horizon in a latosol profile, Zambia (from Webb and Hawkes, 1962; Levinson, 1980).

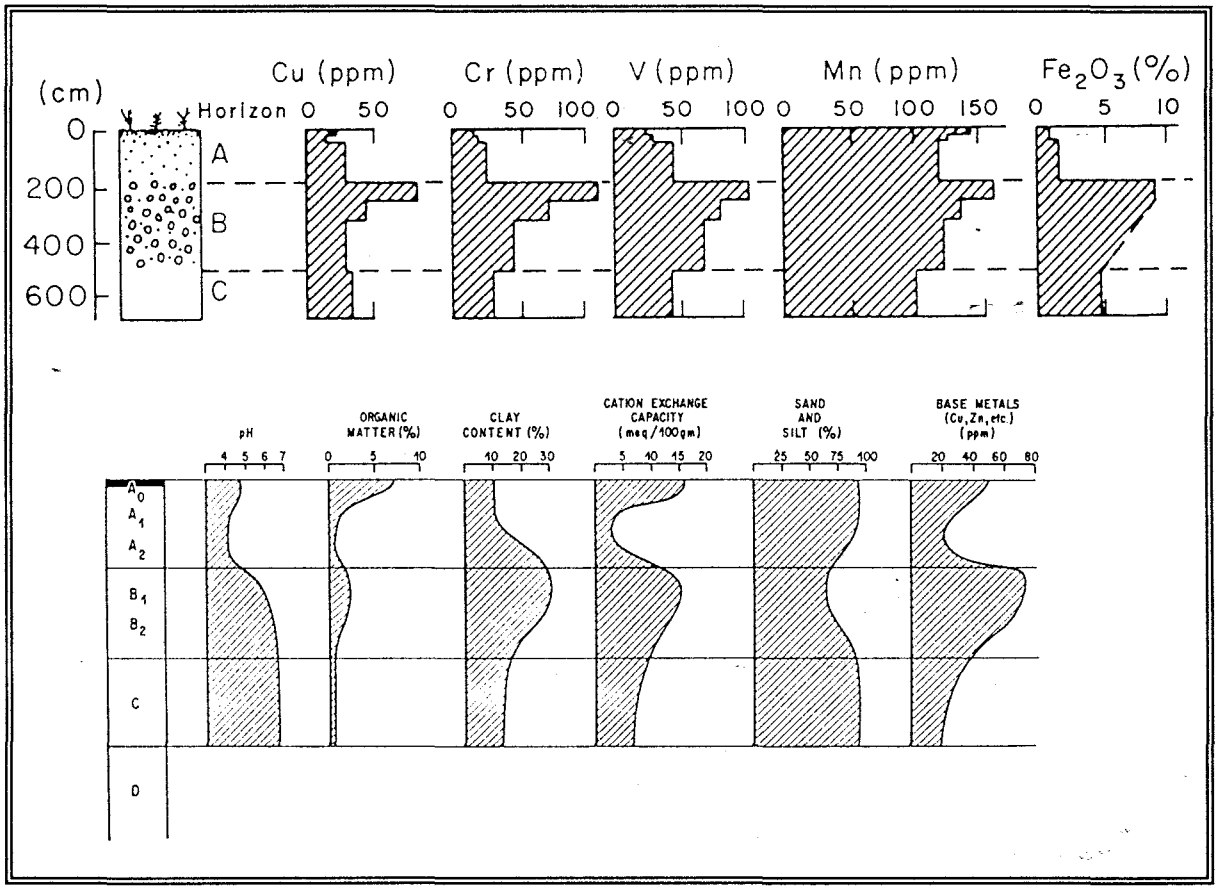

Fig. 5.3: Variation in metal content with soil horizon (from Weeb and Hawkes, 1962; Levinson, 1980 respectively).

The base metals that can be found in a soil profile appear in different forms: cobalt, nickel, zinc and lead occur as more firmly bound exchangeable cations. Copper and to some extent zinc are held in organic or mineral organic complexes; if available, molybdenum is present as an adsorbed base metal in iron oxides (Mitchell, 1972). Since the soil is rich in organic matter, organic complexation plays an important role in adsorption and co-precipitation of base metals. Co-precipitation of base-metals may occur under certain conditions where Fe and Mn oxides are precipitated out of the solution together with clay minerals.

In soil profile, at B horizon the pH starts rising; this fact forces the Fe and Mn oxides as well as the clay minerals to precipitate out from the solution. As a consequence, most of the adsorbed base metals are co-precipitated into this horizon. Analysis to identify the horizon where the best contrast can be identified was carried out in zambian soil (Beus and Gregorian,

1977; after Tooms and Weeb, 1961), Fig. 5.4. From this figure, a secondary geochemical halo formed over copper mineralization can be identified in all three horizons. The highest values in the C layer are related to the anomalous content in the less weathered rock. In the B horizon, the anomalous concentrations of copper are related to the high contents of Mn and Fe oxides, as well as of clay minerals.

A study by Robinson and Carpenter (1979) found that the greatest concentration of copper and zinc in a soil over mineralization occurs in sand-size material in the deepest samples, hosted in limonite, whereas lead occurs in kaolinite throughout the whole profile.

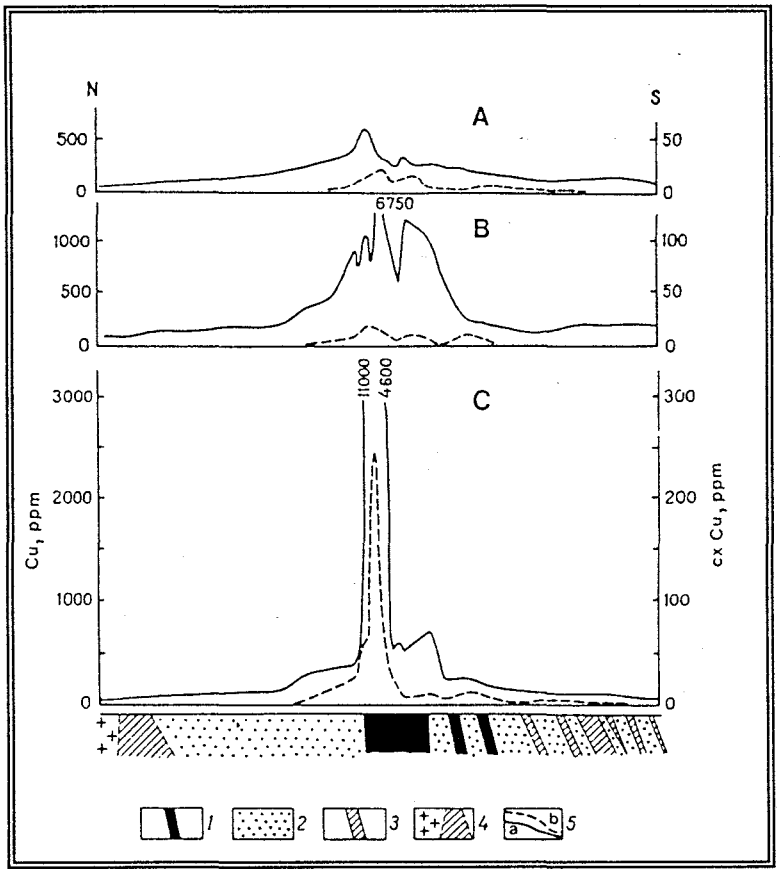

Fig. 5.4: Section showing the contrast in the three soil horizons over copper mineralization in Zambia (from Beus and Gregorian, 1977; after Tooms and Webb, 1961). The lithologies are as follows: 1. copper-bearing ore zone; 2. sandstone; 3. Shales; 4. basement complex; 5. plots of the Cu distribution; (a) total, (b) cold-extractable.

This study suggests that in soil surveys it is particularly important to choose optimum size-depth combination for the maximum contrast, rather than a pre-established horizon and fraction, such as the conventional top of the B-horizon, minus-80 mesh fraction.

Considering the foregoing aspects, base metals appear in the soil profile mostly hosted by specific minerals or Fe, Mn oxides. These may be forced to precipitate when the pH rises at the depth defined as the B-horizon. Nevertheless, the highest contrast have been identified sampling other horizons, provided that a suitable size-fraction has been selected. Hence, for soil surveys, it is particularly important to choose optimum size-depth combination for analysis so as to enhance the contrast.

5.5. EXPLORATION GEOCHEMISTRY IN TROPICAL AREAS

Tropical areas consist of thick residual soil cover and sparse outcrops. Residual soil surveys have been widely applied in such areas either because other methods are too expensive or are technically ineffective. In this context, areas of deep weathering in the Southern Appalachians of USA, East and Central Africa, South America and Northern Australia have been found as suitable for geochemical soil surveys (Rose et al., 1979; Levinson,1980; Smith, 1982; Butt and Zeegers, 1992). Exploration geochemistry in these areas can consists of the following steps aimed at reducing the size of the area until targets can be identified: stream sediment survey, follow-up soil survey, rock- type discrimination, trace element studies in lateritic profiles.

5.5.1. Stream Sediment Survey

Streams and rivers are the principal channels into which the weathering products of rock and their contained ore minerals are channelled. The stream sediment is thus a crude sample of all the weathered material within the drainage basin of the stream. Provided that the stream drains mineralized ground, then, the stream sediments may carry abnormal traces of the ore minerals.

According to the mobility of the element, this can be identified far away from the source. Although in an arid environment, Beeson et al. (1975) identified Zn anomalies as far as 15 km away from the source in Gamsberg, South Africa. Normally zinc is more stable in aqueous solution and coprecipitation is less rapid, occurring with oxides in the more oxidizing

water of the stream itself. Lead in tropical environments forms stable secondary minerals such as phosphates and phospho-sulphates, which may be then dispersed mechanically. This base metal remains less mobile and thus its anomalies will be only in the immediate proximity to mineralization. Molybdenum forms soluble complexes; thus, its dispersion model can be widened by hydromorphic means. The oxidation of molybdenite can produce ferromolybdenite which precipitates near the source.

In stream sediment surveys, special attention is normally paid to Fe and Mn oxides. These oxides scavenge base metals and can enhance the concentration of these metals. Fe and Mn oxides precipitated in poorly drained sediments enhance the concentration of Co, Ni and Zn. In addition, Rose and Suhr (1971) in Chao and Theobalb (1971) indicated that one of the major hosts for Zn, Cu, Ni and Co in stream sediments was found to be Fe and Mn oxides (Table 3.3). Downstream dispersion curves for Zn, Cu and Pb in the black coating compared to that in the minus 80-mesh fractions of the real stream sediments are shown in Fig. 5.5 (Carpenter, 1975). Zinc concentration in the coatings increases from 20 ppm upstream from the mine to over 2500 ppm a short distance downstream. In the minus 80-mesh fraction, values for Zn increase from 45 ppm to only 265 ppm. A similar relationship is indicated for Cu (Fig. 5.5B).

For both cases, the magnitude of the Zn and Cu anomalies is distinctly higher for the coatings than for the minus 80-mesh fractions. The relationship for Pb is different to that for Zn and Cu (Fig. 5.5C). Pb concentrations immediately downstream from the mine are very low in the black coating compared to that in the minus 80-mesh fraction, this fact suggests that lead is not adsorbed by Mn oxides. In addition, the detectability of base-metals mineralization is enhanced by ratios Zn/Mn and Cu/Mn, as well as Zn/Co and Cu/Co, Fig. 5.6 (Carpenter et al., 1975). Data from Butt and Nichol (1979), Nowlan (1979), suggest that an examination of element associations can be an important first step in the interpretation of base-metal drainage anomalies. The following appears to be the principal associations (Butt and Nichol, 1979):

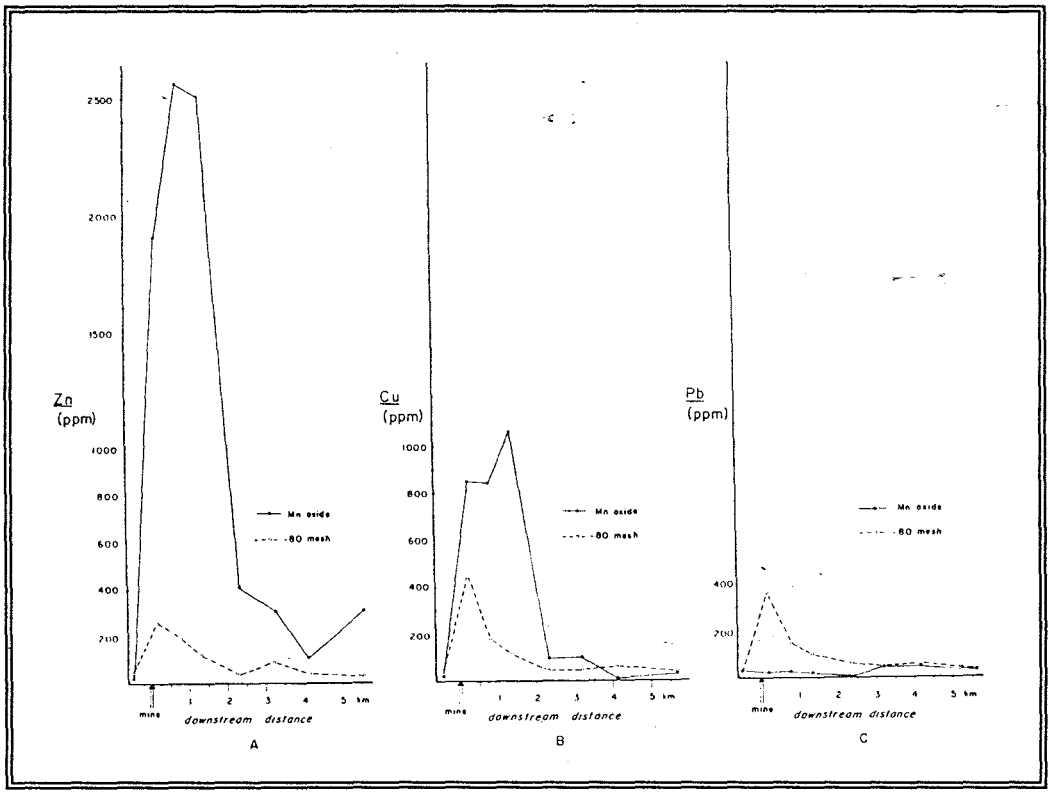

Fig. 5.5: Downstream dispersion curves for Zinc (A), copper (B) and lead (C) in the Magruder mine area (USA), from Carpenter et al., (1975).

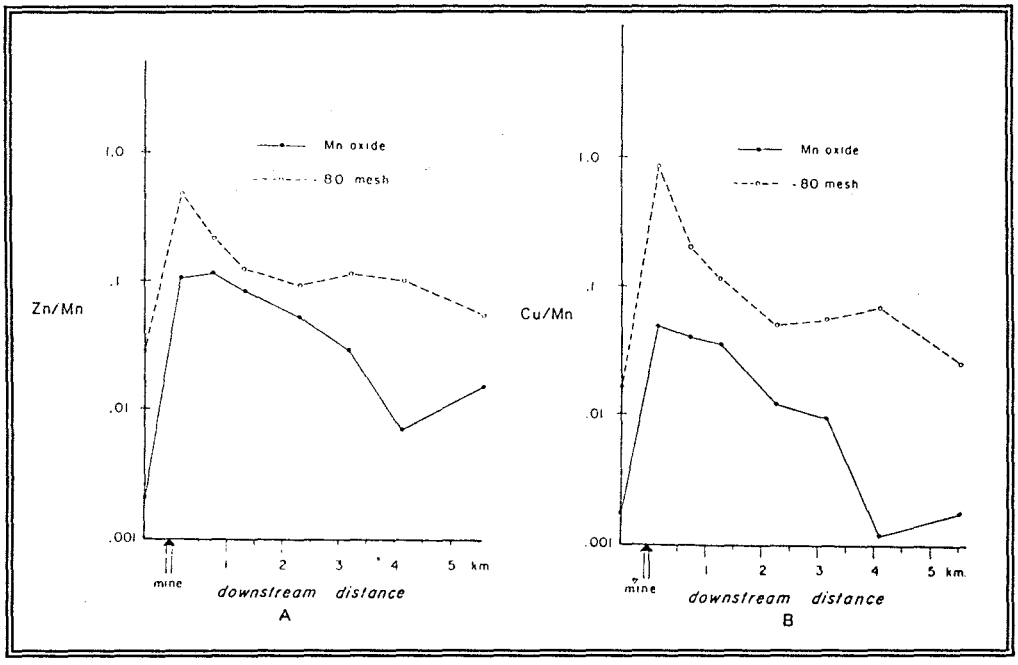

Fig.5.6: Downstream dispersion curves for Zn/Mn (A) and Cu/Mn (B), in the Magruder mine area (USA), from Carpenter et al., (1975).

Predominantly clastic, significant:	Zn, Cu, Pb + Fe, Mn, Co, Mo, As
Predominantly hydromorphic,	
Significant:	Zn, Mn + Fe, Pb, Cu, Ba, Co, Ni, Mo, As
or:	Zn + Mn, Fe, Pb, Cu, Ba, Co, Ni, Mo, As
Predominantly hydromorphic,	
non-significant:	Zn, Mn, Fe, Co + Ba, Ni, As, Mo

Collected samples, in stream sediment surveys, can be heavy minerals, Mn and Fe coatings, organic material and the proper stream sediment samples. Stream sediment surveys are normally carried out in the reconnaissance phase and, if anomalies are identified, follow-up soil surveys are undertaken to cover the whole area the sediments were channelled from.

5.5.2. Follow-up Soil Surveys

A follow-up soil survey should be conducted in selected areas, which normally are of moderate relief. Before the exploration, an orientation survey might be carried out, aiming to determine the existence and characteristics of the anomalies associated with possible mineralization. This consists of soil profile characterization, identification of base metals partitioning, fraction size and the horizon where the highest contrast is possible. For this purpose, samples are normally collected from each horizon including the saprolite; in some areas a complete profile series of samples is taken at critical locations; the objective in this case is to locate a characteristic near-the-orebody profile in which metal content increases or stays constant in going from B to C horizon. Normally it might increase in this direction because the primary ore is being approached (Fig. 5.4), but in samples taken at greater distance from the orebody, the B horizon will generally be richer. This information may be used in selecting adequate prospecting techniques and in determining the factors to be borne in mind during the data interpretation phase (Hawkes and Weeb, 1962). Previous studies are normally done, aiming to identify the fraction which yields the best contrast, so that variations of metal content can be picked up. Table 5.2. presents an example of the concentration of several trace elements

as a function of the grain size, from a lateritic soil profile in Nigeria (Matheis, 1981). In this case, based on a series of orientation studies, a perchloric-nitric acid leach (7:3) of the -200 mesh fraction of soil, collected at upper B-horizon (60 cm) proved to give the most consistent data.

Table 5.2: Relative trace-element distribution in selected grain-size fractions of B-horizon lateritic soil (from Matheis, 1981).

	Recovery	of metal	content	in %	
BS mesh	Co	Cr	Li	Mn	Zn
-200	41.4	39.5	28.6	35.2	42.3
+200 -120	24.1	29.9	25.0	22.4	25.4
+120 -65	17.2	14.7	25.0	21.0	14.6
+65 -35	17.3	15.9	21.4	21.4	17.7

If the orientation study is not possible, then the B horizon is considered the zone of mineral accumulation, the one sampled in geochemical prospecting. Other horizons can be used if the same horizon is sampled at every site.

Considering that contrast can be defined as the difference between the relative abundance of an element related to mineralization and its normal abundance in the barren country rock, contrast in soil samples will be a function of the initial contrast in primary environment, the relative mobility of the element during the weathering process and dilution by barren country rock. It will also be a function of the affinities the element exhibits in the secondary environment and the way it is being held in the sampling horizon. In order to enhance the contrast, each of the steps from sample collection until data interpretation should be carefully designed. Analytical procedures are important in enhancing anomalies in soil surveys. Partial, specific or sequential analytical techniques for determining the mode of occurrence of metals in samples and multielement analysis are some examples (Chao, 1984; Thomson, 1986). These analyses permit the recognition of element associations characteristic of mineralized and unmineralized situations.

The following step, after the orientation studies, aims to elucidate:

(1) Sample material: soil sample collected at specific depth.

(2) Sampling pattern: Criteria for grid layout were clearly discussed by Thomson (1986). Sampling grid should be established in such a way that a minimum of two adjacent samples will be within the geochemical dispersion pattern of any target. Undersampling can lead to uncertainties in interpreting the survey, while, an oversampling will unnecessarily increase the costs.

(3) Sample preparation and analytical procedures: According to the orientation studies, a certain grain size is selected and a specific analytical method is chosen. These are normally established in the light of the highest contrast possible.

(4) Criteria for interpretation of the results: In these terrains, the weathering completely alters the base metal geochemistry, mineralogy and structure of the original bedrock. In general, mobile elements are leached from the system and immobile elements such as Cr, Fe and Al are left as residual accumulations. Elements with intermediate mobility such as Cu, Ni and Co are only partially leached and they tend to be redistribuited within the weathering profile (Butt and Sheppy, 1974). An accurate data interpretation criteria should be able to distinguish, in all residual material, the effects of weathering from those due to bedrock geochemistry. If so, then geochemistry exploration will be successfully used to identify mineralized bedrock from residual soil.

5.5.3. Rock Type Discrimination

One of the tasks of soil geochemistry in tropical environments is rock type discrimination using multielement associations and metal ratios. Examples of this come from Niquelandia, Brazil (Thomson, 1986); Ife, Nigeria (Matheis, 1981); Australia (Hallberg, 1982); French Guiana (Zeegers, 1979) and the Wan-Rumbek area, south Sudan (Zeegers and Lecomte, 1992). The basis for this analysis is that, in tropical environments, outcrops are sparse, if they do exist; normally there is a thick residual soil cover. Multielement associations and metal ratios can be particularly useful in identifying geochemical patterns related to buried rock types. A study by Zeegers and Lecomte (1992) in south Sudan demonstrated that clear

geochemical signatures even where there is a thick lateritic soil, can distinctly identify lithologies such as nepheline-syenite (Ti-Nb-Al-Zn) and basic rocks (Cu-Zn-Al association).

In a deeply weathered terrain it is important to identify soil geochemical criteria for lithological discrimination (Hallberg, 1982). For the majority of igneous rock classes including rhyolite, dacite, andesite and basalt, a plot of TiO_2 vs Zr provides excellent discrimination criteria regardless of the degree of weathering and alteration. Figure 5.7 shows an example of geochemical pattern related to both rock type and mineralization (Thomson, 1986). On the basis of individual metal abundances and distribution patterns it is not always possible to distinguish the source as being either barren ultrabasic rocks (Cu and Ni in silicates) or nickel-copper sulphide mineralization. Using the ratios (Ni/Cu, is commonly used for this purpose) it can be seen where copper is high with respect to nickel (sulphide mineralization) and where nickel is high with respect to copper (ultrabasic rock). From this preliminary geochemical mapping, it would be easy to conduct a comprehensive interpretation of the soil survey, particularly regarding the identification of unusual geochemical patterns/associations that cannot be related to rock types but only to supergene enrichment or specific metals.

5.5.4. Base Metal Studies in Laterite Profiles

The landscapes of tropical areas are typified by the widespread presence of laterites and of the corresponding deep weathering profiles; these, together with the bauxites are special cases in tropical soil profiles. Laterites are known by their distinct layering where a classical iron cap or cuirasse zone can produce outcrops or suboutcrops.

In dissected profiles, a stone line may develop; this horizon is known to concentrate iron pisolites, which develop from the mottled zone. A soil survey in tropical terrains should necessarily pay attention to the distribution of chemical elements in a laterite profile, because this is a common feature. Some base metals are concentrated in the stone line adsorbed by goethite and hematite, others are concentrated in saprolite hosted in the kaolinite or smectite or even forming proper secondary minerals.

Two groups of Ni laterites have been identified: those with high MgO contents and low iron oxides. In this case, the Ni enrichment occurs in the base of the profile in the saprolite, hosted in Mg minerals such as kaolinite; and those with low MgO and high iron oxides

content, for which Ni will be found in the pisolitic layer (Zeissink, 1969). Zeegers (1979) stressed a good correlation between either Ni and Cu with iron oxides (correlation coefficient of 0.5 for both). Cobalt and nickel exhibit the same radii and normally they behave similarly. However, cobalt is strongly concentrated at the upper part of the profile.

Lead presents remarkably constant values along the profile; the same behaviour was described by Zeegers (1979) who classified Pb as an element unaffected by ferralitic weathering; it shows no association at all with iron oxides or any preference in a lateritic profile.

Zinc in the lateritic profile exhibits its high mobility character, and it is difficult to use this base-metal as an important indicator for mineralized bedrock. Smith (1977), identified a close association between Ni, Co and Cu with both goethite and hematite in unmineralized lateritic profile (Fig. 7.4). This work has shown that during lateritization of ultrabasic rocks, Ni is firstly associated with smectite, while Cu is associated with goethite. With further weathering, an association of Ni with goethite occurs, whereas that of the Cu and goethite continues. At a leter stage, as the iron oxide crystals grow in size, the concentration of some elements that were previously associated with iron oxides, such as Ni and Cu are reduced to low levels. According to their behaviour in lateritic profile, base metals have been divided into three groups (Zeegers, 1979; Zeegers and Lecomte, 1992):

(i) elements such as Cu, Zn, Ni, Co, are associated with Kaolinite, smectite or other secondary minerals forming the saprolite. Ni normally appears in garnierite, in the base of the profile. These base-metals are strongly leached when the Fe_2O_3 content increases.

(ii) elements unaffected by lateritic processes, such as Pb.

(iii) elements such as Mo, which have a strong affinity for the oxide. These will be enriched in the Fe-rich horizon.

Lateritic profiles are diversified; they can be developed in savannas or in rainforest environments. The characteristics of the final profile reflect such environments. The discussion above takes into account the normal lateritic profile regardless of specifications related to the environments; such details are considered in Chapter 7.

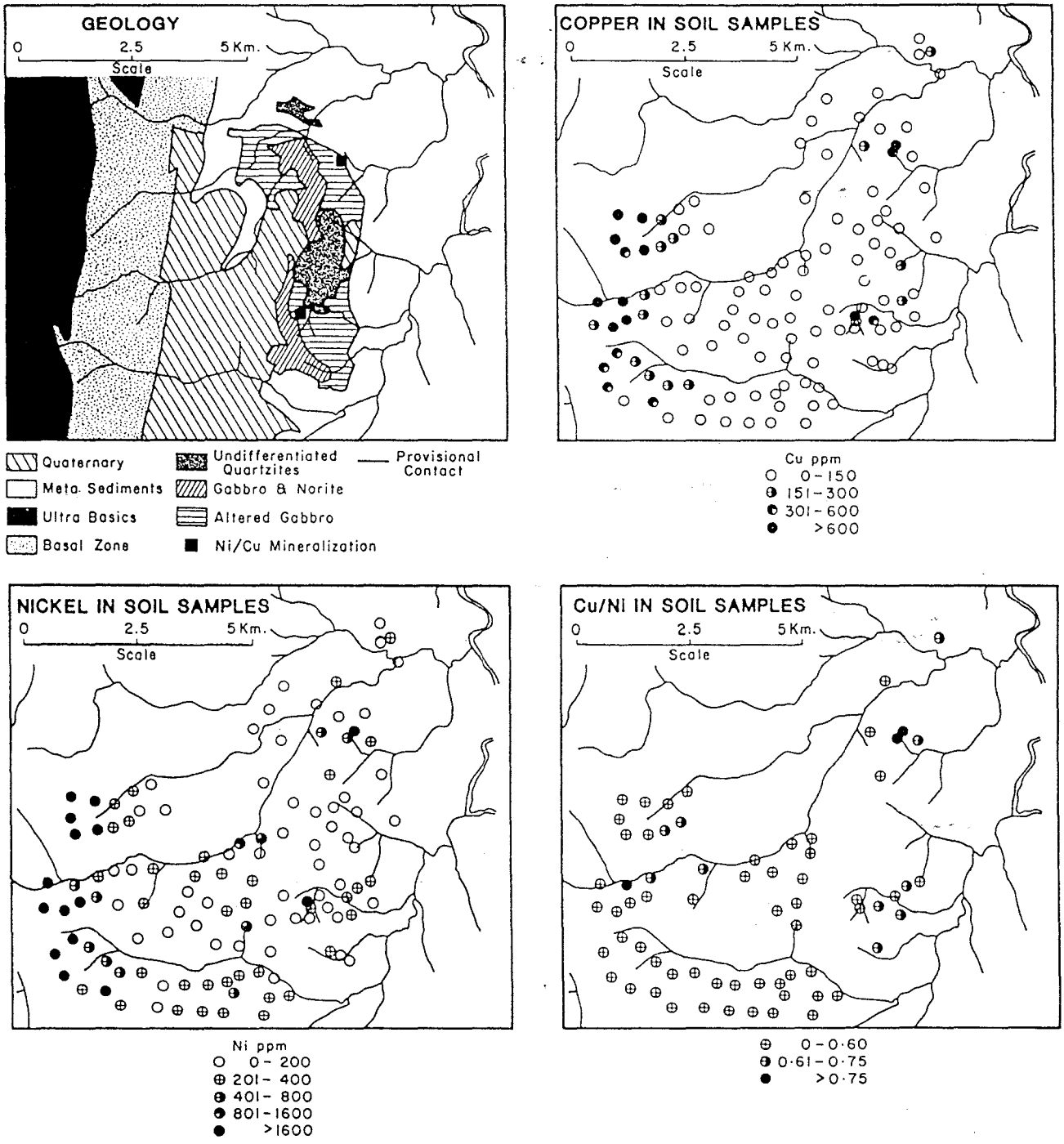

Fig. 5.7: Solid geology, the distribution of copper, nickel and copper:nickel ratios in soil samples (after Thomson, 1986).

6. GOSSAN

6.1. INTRODUCTION

Gossan as a iron rich cap was always recognised as being associated with important mineralizations; there is evidence of gold and copper mined at the surface from outcropping gossans, particularly of the supergene enrichment zone, from long time ago. With intense mining, the superficial deposits became exhausted; together with the improvement in metallurgical processes and mine dewatering techniques, the underlying sulphides have become more important and gossans are sought as an indicators of these underlying mineralizations. However, it has been observed that not all gossans or zones of ferruginization are underlain by important sulphide mineral deposits with significant base metal content. Hence, techniques were sought to distinguish gossan associated with potentially economic mineralization from those which are simply ferruginous outcrops. In this context, macroscopic diagnostic features including colours, textures, boxworks and mineralogy were developed to assess gossan outcrops. Nevertheless, not all gossans exhibiting these diagnostic macroscopic characteristics were always followed by important mineralizations; sometimes their interpretation was even equivocal.

The evaluation of precise geochemical relationship between the sulphides and the corresponding gossan zones of the potential deposits appears to be very useful in classifying the different types of gossan with special reference to their base metal content. Criteria are now available to test and evaluate the potential of a given gossan, if it is particularly underlain by an interesting sulphide mineralization. Special reference is here addressed to works by Blanchard (1944) and Zimmerman (1964) who introduced geochemical evaluation to gossan assessment. According to Taylor and Thornber (1992), geochemical evaluation of gossans is now universally accepted as a cost-effective technique in the exploration for outcropping and near-surface base-metals mineralization, particularly in deeply weathered terrain.

6.2. DEFINITION

In the near-surface weathering regime, most hypogene sulphide mineral assemblages are unstable in the presence of weathering agents, particularly water-dissolved oxygen, carbon dioxide and ionic species. The action of these weathering agents tends to equilibrate the

sulphide body electrochemically and give rise to more stable secondary sulphide and oxide mineral assemblages. The weathering agents, being derived from the atmosphere, generally decrease in concentration with increase in depth below the surface. As a consequence, sulphide bodies generally form vertical zonation, in weathered profiles. Ideally the hypogene orebody grades upwards into a more oxidized zone which may be enriched with ore metals (Figs. 6.1 and 6.2). This zone is overlain by an oxide zone leached of ore metals, itself capped by gossan at surface.

The most critical step in the overall gossan forming processes is the transformation of the sulphide assemblage to stable oxidate assemblage. During this process, the sulphides oxidize to sulphate; the intrinsic metal-sulphur bonds are broken and the released metal cations are either dissolved in the co-existing groundwater or are precipitated as insoluble oxidate minerals. Huge amounts of iron, associated with base metals and precious metals in sulphide form, are fixed below the water-table in new secondary minerals; other metals are partly

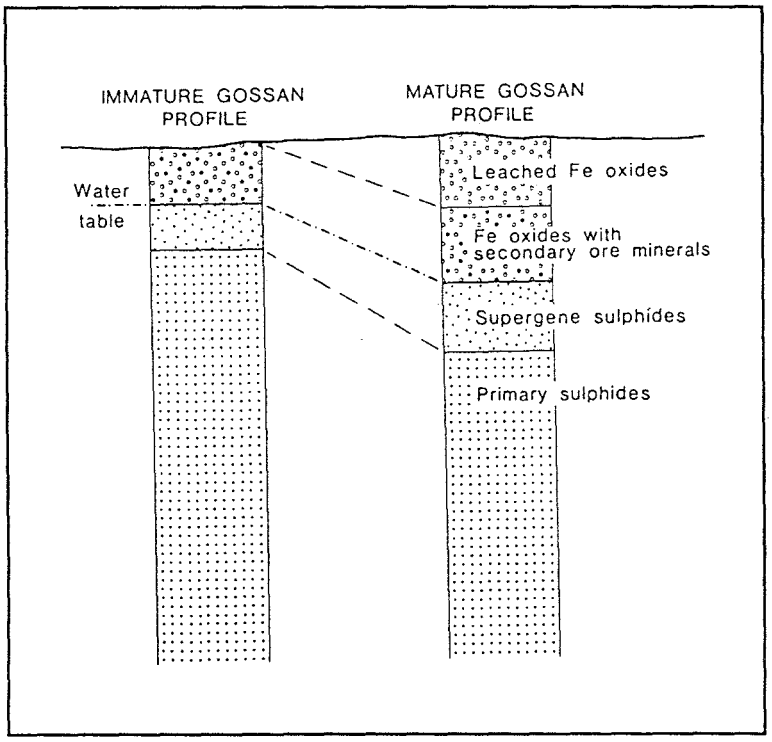

Fig. 6.1: Diagrammatic representation of zonation in mature and immature gossan profile (from Nickel, 1982).

leached away in the groundwater and they are partially precipitated nearby, as oxides, carbonates, sulphates, halides, phosphates or vanadates (Blain and Andrew, 1977).

The residues of iron bearing minerals in the form of goethite and limonite, together with varying amounts of introduced silica constitute the gossan which caps sulphide mineral deposits. The process described above takes place at solid-liquid interfaces provided by cracks, fissures and grain boundaries along which weathering agents can penetrate. According to Thornber and Taylor (1992), three processes need to occur for an assemblage of sulphide minerals to alter to a gossan:

(i) Dissolution of some chemical elements from the sulphides. All of the base metals, at suitable pH and Eh conditions, may be released from the sulphides during this process.

(ii) The oxidation of S and commonly other elements such as Cu, Pb, Mo, Ni and Fe.

(iii) The precipitation, recrystallization and dehydration of minerals to an assemblage that eventually becomes that of the gossan.

The geochemical assessment of gossan is based on these three processes which are well understood; thus, a careful and detailed study of all chemical and mineralogical species and aspects of a gossan can lead to an useful understanding of the nature of the original sulphide mineral assemblage and the concentration of the target elements- the key information to be extracted from a gossan. Commonly, in mineralized terrains where deep and penetrative weathering has resulted in the near surface mobilization of iron and silica, during the time of exposure, and the supergene alteration has obscured the macroscopic evidence, then exploration should be based on chemical evidence.

6.3. THE MECHANISM OF GOSSAN FORMATION

In contrast to almost all silicate minerals, most massive sulphide bodies are coherent electronic conductors, and therefore, the reactions involved in the weathering of such bodies are mostly electrochemical. These reactions take place between the sulphide conductor or semiconductor and the co-existing aqueous media; they proceed by processes similar to the galvanic corrosion of metal alloys (Brain and Andrew, 1977; Thornber and Taylor, 1992). These redox reactions consist of the combination of a reduction reaction at a cathode that consumes electrons, and an oxidation reaction at an anode that provides the electrons that flow within the sulphides from the anode to the cathode (Fig. 6.2).

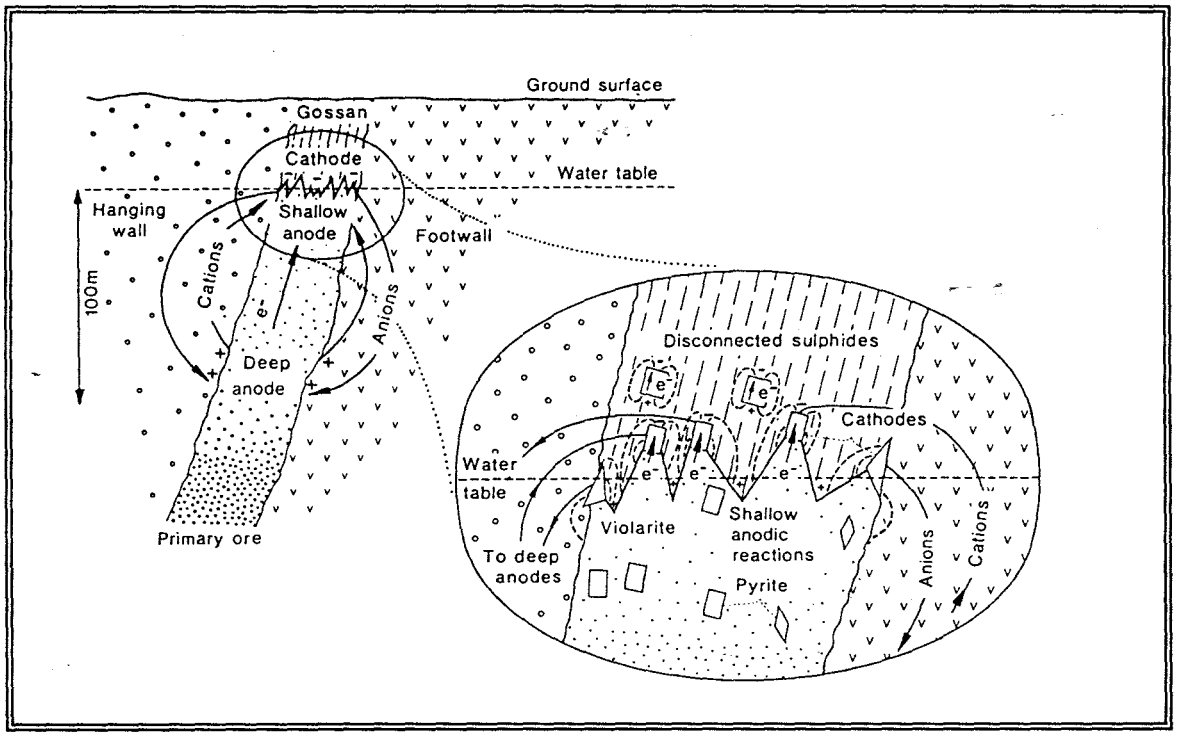

Fig. 6.2: Cross section showing the deep weathering reactions in a sulphide orebody; example from Kambalda Ni sulphide (from Thornber, 1982).

The electrochemical process consists of couples of oxidation-reduction involving the exchange of electrons; the following formula expresses the reactions, if taking place in aqueous media:

$$aA + wH_2O \rightarrow bB + mH^+ + ne^- \qquad (6.1)$$

where ne^- is the number of electrons and other lower case letters specify the number of moles of the participating substances. The process takes place at certain conditions of pH, Eh and the activities (related to the concentration). In this sense it is convenient to describe the geological environment in which sulphides weathering reactions take place in terms of pH vs Eh diagrams at specified ionic activities. It should also be noted that the Eh in the natural environments is controlled by all chemical species present and not vice-versa. The ranges of pH and Eh in the zone of weathering and sulphide oxidation were studied by several workers on this topic (Thornber 1975a,b; Thornber, 1976; Blain and Andrew, 1977; Andrew, 1980; Titley, 1978;

Thornber and Teylor, 1992). The sulphides oxidation proceeds as the orebodies are progressively exhumed and they encounter a zone in the weathering regime where their contained sulphide minerals are no longer stable with respect to co-existing oxygenated groundwater solutions. In releasing electrons, the oxidizing ore becomes positively polarized and forms an anode. At the top of the conducing orebody, dissolved oxygen, in continuously replenished supply in the ground water, is reduced to hydroxyl groupings and the consumption of electrons from base metals oxide them to cations, then soluble. The cathodic reduction of dissolved oxygen can be described as in equation (4.7). The equation (4.7), if combined with the oxidation of a mono-sulphide results as follows:

$$MS + 4H_2O \rightarrow M^{2+} + SO_4^{2-} + 8H^+ + 8e^- \qquad (6.2)$$

where M is a divalent base metal, which is subsequently released as a cation.
These reactions, as described in point 4.4.1., apply to all sulphide minerals, consequently the base-metals are released from the host minerals. The base metals so released may percolate in the form of ion-bearing solutions until the water-table and react with the pre-existing sulphides forming the supergene enrichment zones (Brain and Andrew, 1977). The last step of this mechanism is the formation of stable iron oxides caps composed of goethite, limonite, silica and many other small constituents at the top of the profiles.

6.3.1. The Role of the Water-table

The role of the water-table can be well understood if an initial consideration is given on the processes taking place below the water-table, then at the water-table and above this line.

(a) Below the water-table, conditions become increasigly reducing and alkaline with depth. Measurements made on material from Kambalda (Nickel and Thornber, 1977) indicate pH values between 8 and 9, and Eh values at the order of - 0.3 volts at depth of 100 m below the water-table. The rock below the water-table remains relatively stable, although it becomes enriched in leached metals because of the downward-percolating metals-bearing solutions. Thus, far away below the water-table, primary minerals are stable, but underneath this line, there is a zone of enrichment. All the base metals driven from the leaching zone are

concentrated in this horizon in the form of supergene sulphide minerals (Fig. 6.1).

(b) At the water-table or in the vicinity of it, sulphides and country rock become instable and decompose. The role of pH, Eh and type of country rock have been discussed as important parameters in this process. The decrease in pH at the water-table (Fig. 6.3) can be attributed chiefly to the decomposition of the sulphides and the hydrolysis of Fe-bearing silicates. This pH promotes the oxidation of pyrite and other sulphides (Figs. 6.4 and 6.5). At this stage, base-metals are released and enter the solution as soluble cations; those which are not stable can form secondary minerals and they precipitate. This might be the case for lead which can not find proper conditions to be mobile (Pb is only mobile at pH $<$ 0.4, Fig. 3.8); but other cations such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} are mobile at the weathering conditions.

(c) Above the water-table, there is no a permanent aqueous phase; there is, therefore no way to quantify the geochemical parameters (Nickel and Thornber, 1977). Nevertheless, it is reasonable to admit that the oxidation potential is high since there is an easy access of oxygen. Minerals at this environment are already decomposed and a leached cap develops; silicified goethite and limonite are the common assemblages found in this zone.

From the foregoing it can be suggested that the process of gossan formation occurs mainly at the water-table. Vertical changes in the level of the water-table exert an influence on the type of gossan profile. According to Thornber and Taylor (1992), with a rising water-table, the rate of gossan formation will be limited by a decline in oxygen access and weathering will cease. A static water-table will assist the development of a greater separation of cathodic oxygen reduction and anodic leaching; it will be extended to the point where oxygen reaches. With a falling water-table, oxygen access is ensured; thus, the profile can develop. In this sense, the development of a gossan profile may be considered as taking place during periods of falling water-table. This can be seasonal or due to long term events such as climatic changes or epirogenic movements. During these events, the cathodic, alkaline, oxygen-reducing reactions need to be nearest the oxygen source at the top, and the anodic leaching and acid-producing reactions are developed vertically below. An example of the effect of water-table movement was described by Titley (1978). The profile identified in the Metelen porphyry copper prospect (Fig. 6.3) suggests that two water-tables have prevailed, according to the

supergene enrichment zones in this profile. An early one at A was responsible for the formation of the old enriched zone and a later one at B localizing the present blanket. Although the drop of the water-table permits current oxidation-destruction of the old blanket, this can still be identified as such in this profile.

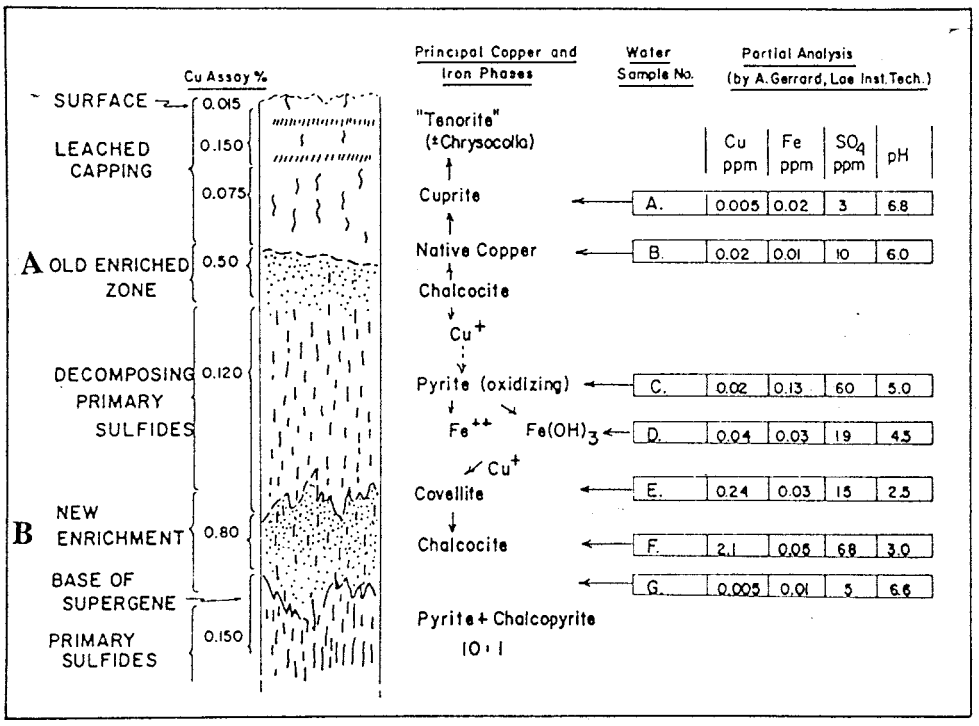

Fig. 6.3: Profile indicating two enrichment horizons as a function of the water-table, example from Metelen escarpment (New Guinea) porphyry copper prospect (from Titley, 1978).

6.3.2. Role of The Ore and Country Rock Mineralogy

The composition of the sulphide ore, as well as of the country rock and the progressive geochemical changes during supergene alteration have a fundamental influence on the ultimate composition of the equivalent gossan. The sequence of sulphide alteration and the geochemical environment in the oxidation zone are important parameters on the development of base metals gossan. During the sulphides leaching processes, base metals such as Cu, Pb, Zn, Ni and Co are dissolved as cations, together with ferrous Fe. According to Thorneber and Taylor (1992), in many ores, Fe is the dominant cation which can precipitate as Fe hydroxide or oxyhydroxide. Base metals can be bound onto these precipitates in terms of adsorption or they can even co-precipitate, following the precipitation of these iron oxides. This process will be

favoured by high pH, therefore, a sulphides rich ore will exhibit low precipitation of either iron or concomitant base metals.

A massive sulphide assemblage with high proportion of Fe sulphides minerals will produce highly acidic weathering conditions; as a consequence, a highly leaching environment will be developed at the vicinity of these sulphides, then only a small proportion of ore elements can be retained in the gossan. However, elements such as As, Sb, Se, Te, W and Mo which form anions may remain with the ion minerals (Thornber and Taylor, 1992). If the mineralogy of the country rock is such that K and Al rich silicates are weathering, then alunite-garosite minerals should be expected. Taking into account the chemistry of these minerals, a wide range of trace elements leached from the gossan can be incorporated in specific sites. The relevant elements found in these minerals are Pb, Fe, Cu and Zn (Scott, 1987). This is an important feature in gossan assessment; if it is suspected that the gossan was formed under acid conditions from massive sulphides, with a silicate country rock, then evidence of the base-metal sulphides that were originally present may still remain. It could be suggested that in such cases, a careful search for minerals derived from the gangue or country rock, precipitated in solution channels or wallrock can supply crucial indications on the composition of the precursor sulphides.

The role of the country rock is also evident when carbonates hosted sulphides are weathering; in this case, the carbonates act as an alkaline buffer and keep the pH higher in their vicinity; therefore, the precipitation of Fe oxydates is very likely to occur and base metals will be incorporated in co-precipitation or adsorbed because this is favoured at high pH. Since the leaching effect of some sulphide minerals is inhibited in these conditions, most of the primary features of the base metals sulphides will be preserved. In fact, the ore minerals have a major influence on the development of gossan because they determine the leaching effect of the environment supplying both iron and Sulphur. The reactive gangue minerals such as carbonates and mafic silicates variously inhibit the process increasing the pH; this promotes the preservation of base metal sulphides features. The initial mobility of trace elements as a function of Eh-pH parameters is crucial and evident in gossan geochemistry; very mobile base-metals will be scarce in a gossan than lesser mobile. The adequate assessment of these parameters from the present composition of a gossan will help to determine the composition of the primary sulphide source.

6.4. CLASSIFICATION OF GOSSANS

In base metals exploration, it is frequently necessary to evaluate the economic significance of an exposed gossan, so as to find out if it is related to any potential sulphide deposit or not. This requires a distinction to be made between the real gossan and other rocks of similar appearance. All the rocks occurring at or near the surface as a hard iron-cap are known as ironstone. Following Blain and Andrew (1977), in mineral exploration, it sounds practical to term all ferruginous rocks "ironstones" until such time as any feature of a true gossan has been recognised. Wilmshurst and Fisher (1982) divided the ironstones into two groups:

(i) Gossan, which are related to sulphide mineralization and,

(ii) Non-gossanous, those ironstones which are unrelated to sulphide mineralization, Fig. 6.4.

Moeskops (1977) developed a model depicting the spatial relationship between true and false gossans, Fig. 6.5; in its scheme, there is always a genetical relationship between these two ironstones. A genetical classification of ironstone has been developed by various authors (Blain and Andrew, 1977; Moeskops, 1977; Andrew, 1980; Wilmshurst and Fisher, 1982); the following is a summary of this classification:

1. Base metals sulphide gossans: they may appear as outcropping gossans, subsurface gossans or masses of ferruginous rock adjacent to a gossan. Like other ironstones, they are variably silicified, chemically stable, refractory and commonly form linear ridges. According to the base metals hosted, they can be subdivided into three broad subgroups: Cu-Zn sulphide gossans, Pb-Zn sulphide gossans and Ni-Cu sulphide gossans. The field relationship can elucidate the economic potential of a gossan; for instance, in Southern Africa, the association of a gossanous horizon in ferruginous exhalative with stratiform barite and aluminous metasediments is a diagnostic feature of a volcanogenic sulphide mineralization (Andrew, 1980). These gossans, as seen in Gamsberg, are typified by hard silicification with various shades of red, dark brown, and black. Because of the their maturity, there are no surface boxworks associated with these gossans.

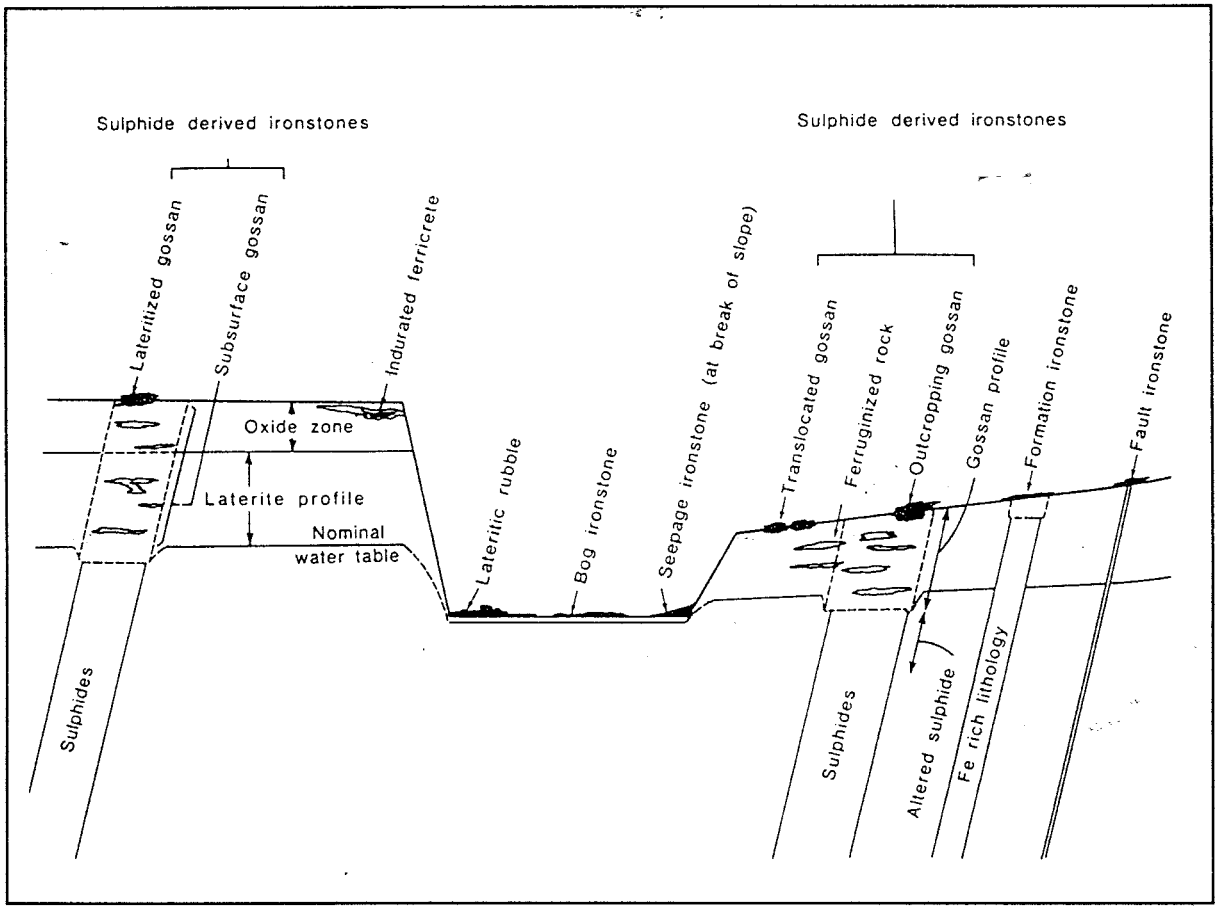

Fig. 6.4: Types of ironstone as classified by Wilmshurst and Fisher (1982).

In general this class of gossans can be identified on the basis of their colours, mineralogy and textures. This example shows that for each group of base metal sulphide gossans there are specific field and geochemical signatures associated with their path of formation. These features are crucial in field and laboratory gossan evaluation.

2. *Iron sulphide gossans*: These are mostly derived from barren pyrite and pyrrhotite mineralization and are difficult to distinguish from true base metal gossans in the field. In fact the gross configuration, large scale textural features and the effect of supergene weathering are

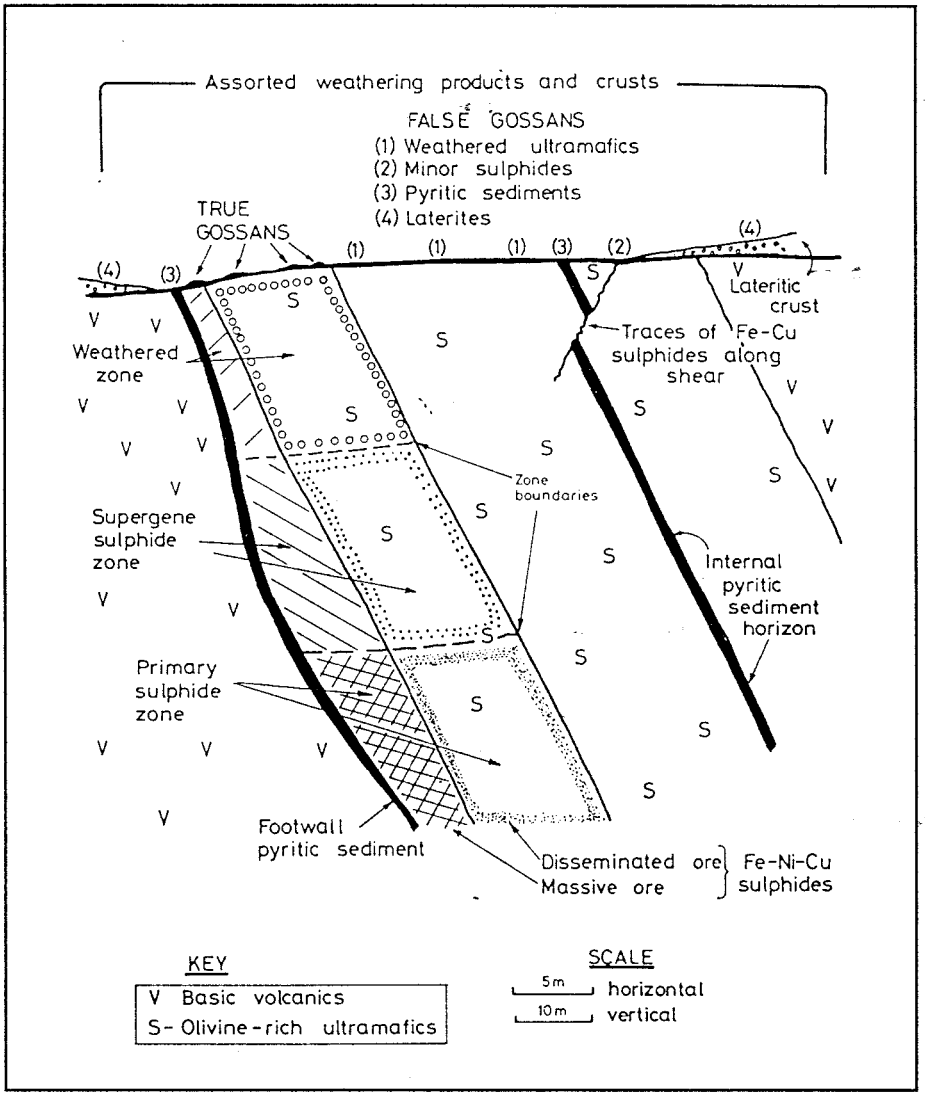

Fig. 6.5: Schematic, vertical section through typical Yilgarn nickel sulphide deposit showing true and false gossans (from Moeskops, 1977).

all common to these two groups. Since the field expression of all sulphide-derived gossans is superficially similar, emphasis should be laid on oxidate mineralogy, because the secondary minerals reflect the elements available during the supergene alteration of these sulphides. Replica textures and geochemical appraisal will then afford their correct genetic classification.

3. Transported gossans: Generally transported gossans range from gossan breccias and loosely cemented scree to massive colloform or columnar accumulations of goethite, hematite

or even manganese minerals. Breccias are normally formed by mechanical transport of clasts which are subsequently cemented by an iron oxide matrix at or near the surface. Most of the transported massive, colloform and columnar types probably are formed by the chemical migration and precipitation of iron as limonite outside the primary ore body source, developing to bog ironstone (Fig. 6.4). These, can be recognised by their exotic matrix and the lack of lateral continuity. Should the above criteria not be satisfactory, then geochemical criteria might be applied.

4. Indurated ferricretes: This type of ironstone occurs generally in deeply weathered lateritic terrains, where the near surface accumulation of iron has formed a hard, indurated duricrust. The subsequent erosion of this blanket may cut through to a greater or lesser extent. Lateritic profiles may be distinguished from the accumulation of pisolithic concretionary structures which are not common in normal gossans; although in places they may be blocky. Ferruginization normally follows the bedding and foliation planes, although in some cases it is transgressive. Again, the geochemical features of this class of ironstone are diagnostic. Where the genesis of gossan or laterite is not apparent in the field, then a detailed investigation of the mineralogy, textures or geochemistry may assist in its interpretation.

Three general groups of factors control the concentration of elements in an ironstone:

(i) Ironstone genetic style, referring to the environment and manner in which the Fe oxides precipitated.

(ii) Profile control, referring to the changes in behaviour of the elements through the oxidation or weathering profile.

(iii) Primary elementary composition, considering the initial composition of the ironstone.

6.5. THE MINERALOGY AND GEOCHEMICAL ASSOCIATIONS OF BASE METAL GOSSANS

The mineralogy of most gossans is dominated by limonite and silica in mutually antipathetic abundance. Limonite in this context refers to amorphous, colloidal iron oxides or finally crystalline goethite with subordinate admixed silica, hematite and jarosite, lepidocrosite, or manganese oxides in various proportions (Blain and Andrew, 1977). The macroscopic recognition of ore-metal oxidate assemblages in gossans may allow immediate preliminary evaluation of the outcrop in the field. The immediate step is the identification of accessory residual minerals in gossan and or ironstone using optical microscopy; residual quartz mostly encloses traces of residual sulphides which could lead to the inference of the primary sulphide mineralogy and lithologic association. In metamorphic areas, relict spinels, basically gahnite ($ZnAl_2O_4$), could be identified from its green colour and can suggest a protolith of exhalative origin. The mineralogy of the country rock can provide indications related to the original sulphides.

Oxidate minerals in gossans are composed of carbonates, sulphates, phosphates and silicates. Some of these, because of their high solubility, are not expected to be preserved during gossan formation. Base metal gossans are normally divided according to their original sulphide mineralization and thus their geochemical characteristics. In an exploration programme the objective of geochemical evaluation is to assess the significance of specific trace elements thus affording the genetical classification of the gossan and when possible the composition of the precursor sulphide. The evaluation assigns, in this way, an unknown gossan to a specific group according to its geochemical signature. The geochemical evaluation of a base metal gossan should take into account not only the identified mineralogy and the trace elements, but also any signature which could help to decipher the possible continuity of this gossan to a primary mineralization.

6.5.1. Copper-zinc Sulphide Gossans

The main primary copper minerals are chalcopyrite and bornite. At the oxidation zone, these can oxidize to malachite, azurite and goethite; if enough silica is available, silicate copper minerals may form including crysocolla and dioptase. Covellite may appear as an intermediate product of the chalcopyrite oxidation and idaite as the intermediate product for the bornite oxidation (Sillitoe and Clark, 1969). The zinc oxidate minerals are poorly

represented in these gossans because the supergene chemical environment does not favour their formation (Blain and Andrew, 1977); this is one of the reasons why zinc released from sphalerite does not appear in the enrichment zone in Fig. 6.6. Copper-zinc sulphide gossans are typified by those distinctive secondary copper minerals such as malachite, crysocolla and azurite. Although less common in tropical areas, minerals such as chalcanthite, green antlerite, blackish green brochantite and cuprite are examples of the oxidation of Fe-poor but copper rich sulphide assemblages (Table 6.2). The oxidation of chalcopyrite to normal covellite is the dominant copper source; early breakdown of chalcopyrite in the alteration sequence could be identified from the manner in which covellite rims with sphalerite and pyrite (Andrew, 1980). Chalcopyrite commonly alters directly to digenite and further to chalcocite (Fig. 6.6). Diagnostic geochemical signature is defined by high Ba-Au-Ag/low Mn association. In the Southern Africa copper-zinc gossans, diagnostic features include high Cu-Pb-Ba/low Mn-Ni-Co-Cr (Andrew, 1980).

6.5.2. Lead-zinc Sulphide Gossans

Taylor and Thornber (1992) divided these gossans into two broad groups:

(1) The sedimentary exhalative Pb-Zn-Ag sulphide gossans; these are further divided into two restricted subgroups: the Mount Isa type (the best examples are in Australia and Canada) which are associated with abundant iron sulphides, and the Broken Hill and Gamsberg type (the best examples are in Australia and South Africa), characterized by an association with Mn-rich quartz-magnetite-apatite-garnet and banded iron formation. The common geochemical association in these groups includes Pb-Zn-Ag-As as major constituents and Co-Ni as minor constituents. The diagnostic geochemical signature for these gossans is the high Pb-Zn-Mn-Ag content.

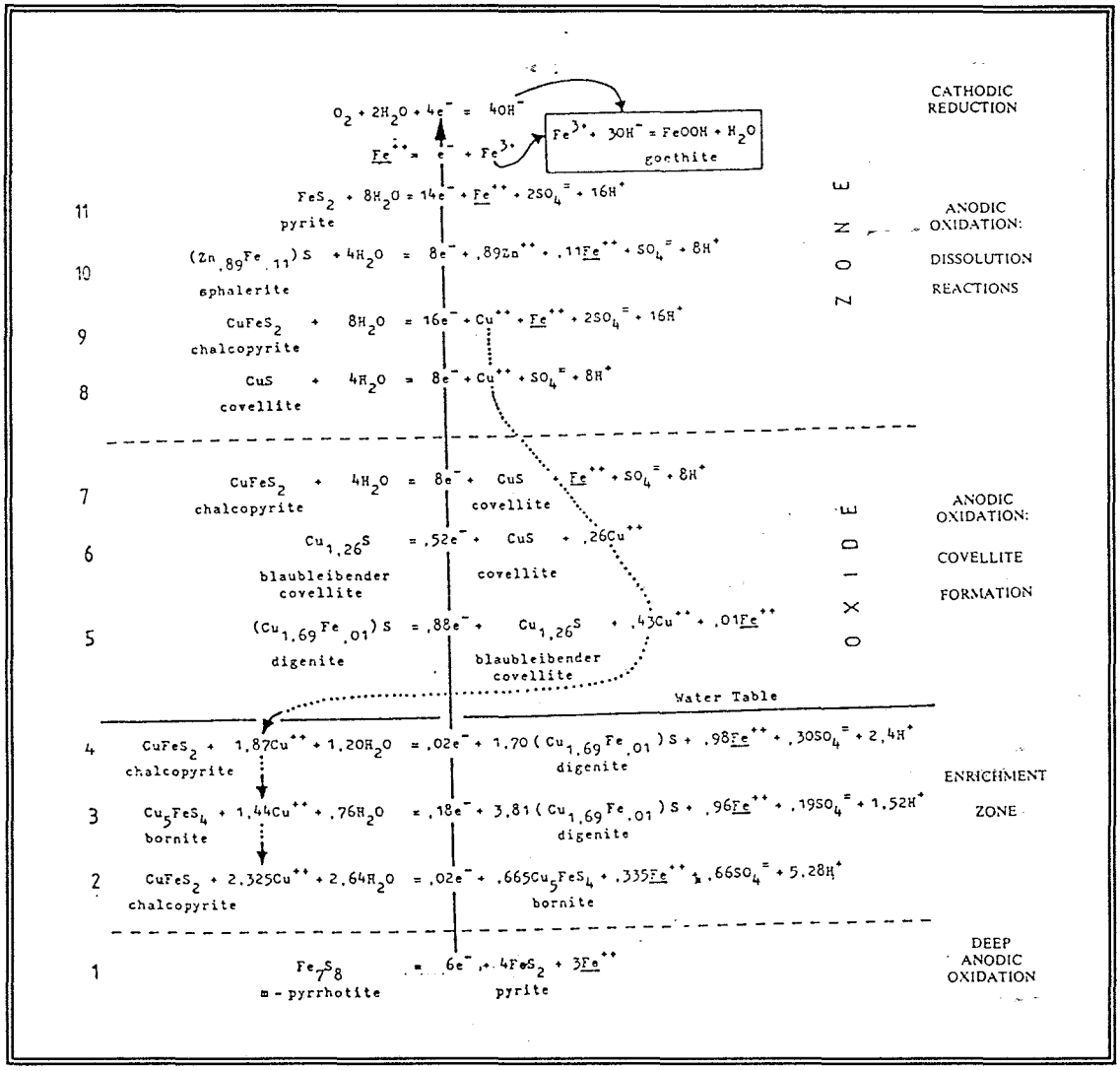

Fig. 6.6: Chemical reactions depicting supergene alteration of Cu-Zn sulphide minerals (from Andrew, 1980).

(2) The carbonate-hosted sulphide gossans. This group was well characterized by Takahashi (1969) and Southwood (1986). Cerussite and anglesite are the common secondary lead minerals, but massicot, minium and plattnerite may occur. Smithsonite, hydrozincite and some times hemimorphite are the common zinc secondary minerals (Table 6.2). The geochemical association is very limited with only Pb-Zn-Cd (Southwood, 1986).

As galena is a very resistant mineral to weathering, so, in young gossans it is more likely to have hard crusts of cerussite staining while other minerals are leached out. The low

solubility of lead allows it to combine with phosphates, arsenites and other anions to form a variety of complexes and insoluble compounds such as plumbogerosite which may be retained in or close to the gossan. Some lead-zinc sulphide deposits, especially those not in carbonate rocks, have well-developed profiles, consisting of a cerussitic silicious gossan below the surface, an oxide zone dominated by cerussite-smithsonite-silver halide assemblage and a cerussite-enriched zone with varying amounts of smithsonite, anglesite, silver sulphosalts and residual sulphides. The depth to primary sulphides varies from 70 to 100 m below the surface (Blain and Andrew, 1977).

6.5.3. Nickel-copper Sulphide Gossans

The nickel-copper sulphides are associated with ultramafic rocks, typically in greenstone belts. The best examples of these sulphides are reported elsewhere (Nickel et al., 1974 and 1977; Blain and Andrew, 1977; Andrew, 1980). Pentlandite weathers pseudomorphically to the more oxidized Ni sulphide violarite (Fig. 6.7) in the deeper zone of weathering sulphides (Nickel et al., 1974 in Thornber and Taylor, 1992). In the hexagonal pentlandite-pyrrhotite assemblage which is characteristic of the disseminated sulphides, pentlandite is converted to violarite and pyrrhotite reacts with the remaining Ni as to form a secondary pyrrhotite which appears along the grains and fill fractures (Nickel et al., 1977). Pyrrhotite itself has numerous crystal forms and all are reactive; the secondary pyrite or marcasite are the normal products of these reactions. Taking into account that these products are from solutions, they will normally appear in fractures and in grain boundaries, together with the secondary pyrrhotite. According to the characteristics of the country rock, the leached cap can present typically nickeliferous gossanous minerals such as morenosite, gaspeite and annabergite (Table 6.2).

The typical geochemical association in these gossans includes Ni-Cu-Ag-As-Co-Cr-PGE, among the less abundant elements. Diagnostic features are given by high Ni-Cu and Pd-Pt contents as well as low Cr-Mn-Zn-Pb contents.

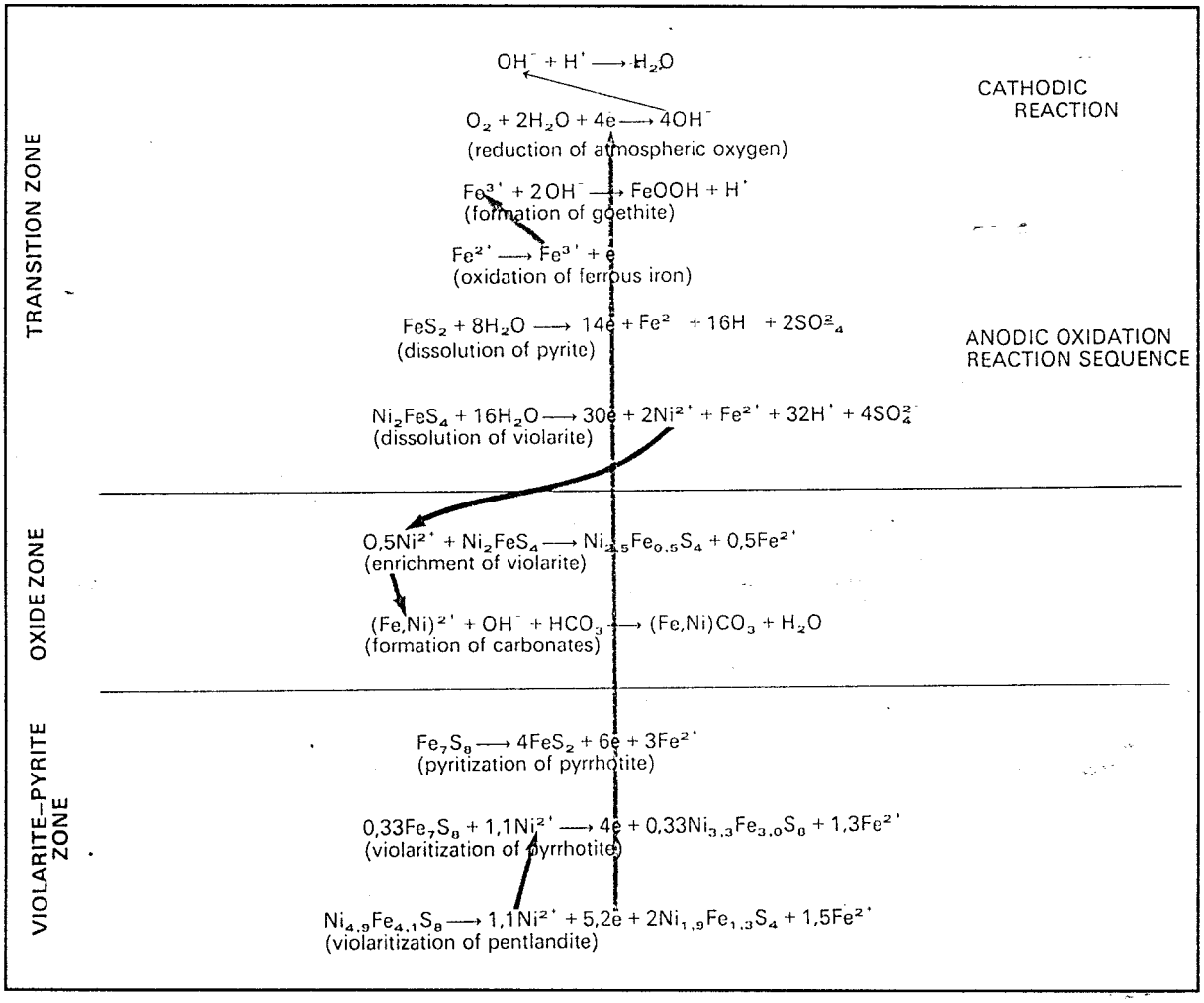

Fig. 6.7: Chemical reactions depicting supergene alteration and enrichment in Ni-Cu gossans (after Blain and Andrew, 1977).

Table 6.1: Summary on the geochemical association of the most common base metal gossans (from Taylor and Thornber, 1992).

Host rock	Expected mineralization	Geochemical Association
Mafic-ultramafic volc.	Ni-Cu	Ni, Cu, Co, Pt, Pd, Ir, Te
Felsic volcanics	VMS Cu-Mo-Au	Cu, Pb, Ag, Au, As, Sb, Bi Cu, Mo, Au, Re
Sediments	Pb-Zn-Ag Cu	Pb, Zn, Ag, Cu, As, Hg, Sb Cu, As, Pb, Sb, Ag, Hg
Carbonates	Pb-Zn	Pb, Zn, Cd

Table 6.2: Common oxidate minerals occurring in base metal gossans (from Brain and Andrew, 1977; Andrew, 1980 and Thornber and Taylor, 1992).

	Iron	*Nickel*	*Cobalt*	*Copper*	*Lead*	*Zinc*
Sulphate	Jarosite $Kfe_3(SO_4)_2(OH)_6$ Melanterite $FeSO_4.7H_2O$	Morenosite $NiSO_4.7H_2O$	Bieberite $CaSO_4.7H_2O$	Chalcanthite $CuSO_4.5H_2O$ Antlerite $Cu_3SO_4(OH)_4$ Brochantite	Anglesite $PbSO_4$ Plumbogerosite $PbFe_6(SO_4)_4$ $(OH)_1$	**Goslarite $ZnSO_4.7H_2O$**
Arsenite	Scorodite $FeAsO_42H_2O$ Simplesite $Fe_3(AsO)_28H_2O$	Annabergite $Ni_3(AsO_4)_2$ $8H_2O$	Eritrite $Co_2(AsO_4)_2$ $8H_2O$	Olivinite $Cu_2AsO_4OH_3$ Clinoclase $Cu_3AsO_3(OH)_3$	Mimetite $PbCl,Pb_4$ $(AsO_4)_3$	
Oxide	Goetite Lepidocrosite (FeOOH) Hematite		Heterogenite (CoOOH)	Cuprite Cu_2O Tenorite CuO	Massicot PbO Litharge PbO	**Chalcophanite $ZnMn_2O_52H_2O$**
Carbonate	Siderite $FeCO_3$ Ankerite	Gaspeite $(Ni,MgFe)CO_3$		Malachite $Cu_2CO_3(OH)_3$ Azurite $Cu_3(CO_3)_3(OH)_2$	Cerussite $PbCO_3$ Phosgenite $Pb_2CO_3Cl_2$	**Smithsonite $ZnCO_3$ Hydrozincite $Zn_5(CO_3)_2O(H)$**
Silicate				Crysocolla $CuSiO_32H_2O$ Dioptase $CuSiO_2(OH)_2$		**Hemimorphite $Zn_4Si_2O_7(OH)_2$ H_2O**
Halide				Atacamite $CuCl_23Cu$ $(OH)_2$	Phosgenite $PbCO_3PbCl_2$	
Phosphate	Vivanite $Fe_2(PO_4)_28H_2O$			Pseudomalachit $Cu_5(PO_4)_2(OH)_2$ H_2O	Pyromorphite $PbClPb_4(PO_4)_3$	
Molybdate	**Ferrimolybdenite Fe_2Mo_3 $O_{12}8H_2O$**			**Lindgrenite $Cu_3(MoO_4)_2$ $(OH)_2$**	**Wulfenite $PbMoO_4$**	

6.6. THE TEXTURAL FEATURES OF BASE METAL GOSSANS

The textural expression of any sulphide as a gossan is a result of the action of different meteoric factors. The roles of ore composition, pH, Eh and country rock have been already discussed. It was also stressed that each sulphide exhibits a proper path of decaying with very specific products. In the same way and as a consequence of the crystallography of each sulphide, a very characteristic texture can be identified. The technique of textural interpretation of gossan was initially developed in North America when Blanchard developed a compressive textural description basically for limonite as the product of different sulphides (Blanchard and Boswell, 1925; 1930). In other words, they interpreted a wide variety of cruciform aggregates of limonite as being textural diagnostics of the different parent material. Since then, textural analysis of gossan has been used as a preliminary field and laboratory evaluation of gossan.

The basis of the textural interpretation of the gossans is inserted on that, during the sulphide weathering process, the bonds between sulphur and cations are broken and new minerals are formed. These new species might be crystallographically controlled by the pre-existing ore mineral. This preservation of ore textures is commonly promoted by in-situ precipitation of iron and silica as the ore is oxidizing (Blain and Andrew, 1977; Andrew, 1980; Taylor and Thornber, 1992). This is a very delicate process which takes place only when there is no corrosive perturbation during the gossan formation. Fortunately in many gossans there is at least a partial preservation of sulphide mineral-replica textures, which are known as "boxworks". As explained (Blanchard and Boswell, 1930; Blain and Andrew, 1977), and documented by Andrew (1980), Fig. 6.8, many minerals at the incipient stage of oxidation, preferentially alter along specific crystallographic planes, grain boundaries, cleavages, parting planes and twin boundaries. The alteration products, limonite and introduced silica, develop continuously along those weak planes forming a network of interlocking septa. Even with subsequent leaching of all the retained sulphides, the early formed septa may persist as a delicate boxwork, a feature classically associated with gossans.

Blanchard and Boswell (1925) identified several types of limonite as a function of the site where it was found and the possible place of formation. This was important in the sense that only in situ gossan can be related to a primary sulphide occurrence. The diagnostic configuration of cleavage boxworks in these sulphides is defined at the initial stage of

oxidation where thin septa of hematite or even goethite precipitate along those weakness planes in sulphide crystals.

In the high Eh-low pH environment near the base of the oxide zone, in situ precipitation of goethite is not favoured, but in the narrow cleavage cracks within predominantly unaltered sulphides at depth, the Eh will be lower and the pH high, precipitation of either goethite or hematite is favoured in such conditions. Only during that short period before the mineral grains become an open system through progressive corrosion along the cleavage will these minerals precipitate simultaneously. This can take place in suitable acidic conditions during anodic oxidation reactions (Fig. 6.7). The occurrence of goethite in boxworks may suggest the conditions in which the sulphide weathering process took place, that is how these boxworks have been used to infer the geochemical environment in the zone of oxidation. They have been also used as an indications of primary sulphide minerals and their interpretation leads to the discovery of many deposits, especially in deeply weathered environments.

Table 6.3: Description of diagnostic replica textures in base metals gossans (extracted from Blain and Andrew, 1977; Andrew, 1980).

Mineral	Control (planes)	Replica tertures	Mineral	Control (Planes)	Replica textures
Pyrite isometric	(100) (100)	Cubic boxworks. pseudomorphs or cavities; Concentrically zoned webworks	Galena isometric	(111) (100)	Regular, cubic, thin walled concntric boxwarks more regular than py. Steeped pyram. boxwork
Marcasite isometric	(110) ((110)	Radial elongate boxworks with bifurcating walls and herring-bone cross walls.	Sphalerite isometric	(110) (111)	Angular well connected boxworks with oblique angles; angular boxworks with with low angle.
Pyrrhotite Hex/Monoc	(0001) (001)	Broadly hexagonal boxworks with hierogliphic cells Closely spaced, parallel, thin wall, celular boxworks.	Molybdenite Hexeg.		Foliated, thin walled boxworks with smoth, rounded walls; casts of original intertices.
Chalcopyrite tetragonal	(111,201) (111,201)	Rectangular boxworks with closely soaced, parallel cell wall and cross walls at 95-110 degrees. Coarse quadrangular, equidimensional boxworks,often thick walled.	Magnetite isometric	(111) (110)	Elongated external forms with closely spaced, parallel septa. Octahedral pseudomorphs ideally acute angles.
Bornite isometric	(111)	Spherical triangular boxworks.	Goethite Orthorombic		Spherical, cellular boxworks; poorly connected hierogliphic boxworks.
Tetrahedrite isometric		Sinous, trench-like countor boxworks.	Siderite Hexagonal	(1011)	Curved rhomboedral boxworks or pseudomorphs.
Pentlandite isometric	(111)	Thin walled octahedral boxwork or pseudomorphs. Feathery margin developed after violarite along basal plane of original pyrrhotite.	Calcite Hexagonal	(1011)	Highly regular, rhomboedral boxworks or pseudomorphs.

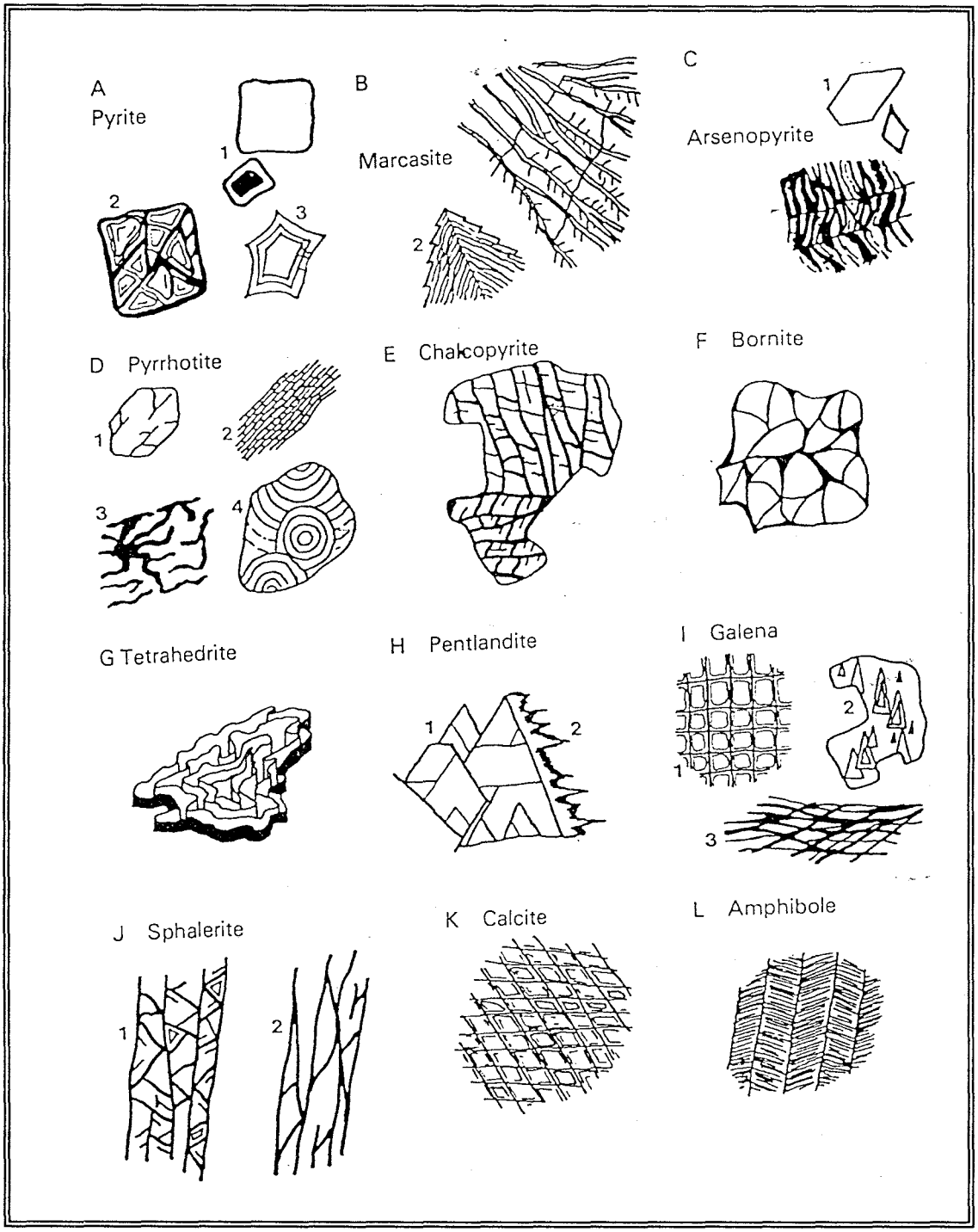

Fig. 6.8: Selected diagnostic replica textures of base-metals minerals and some country rocks minerals (from Andrew, 1980); the description is given in Table 6.3.

6.7. GEOCHEMISTRY EXPLORATION OF BASE METAL GOSSANS

The two most important mesoscopic features in gossans are the mineralogy and the replicate fabric which were described previously. The identification of such textures and accessory or trace residual minerals may help in the characterization of the primary mineralization and lithologic association. The oxidate minerals given in table 6.2 are even more diagnostic and specific, although some of them cannot be maintained so stably during the subsequent gossan alteration.

These macroscopic and mesoscopic diagnostic features can lead to gossan recognition and differentiation from other ironstones only where lower levels of the gossan profile are exposed or even where the gossan is immature and, the features are still preserved. However, these features may be absent or obliterated where the gossan is mature and highly leached or it has been flooded with silica solution, Fe-oxides or other secondary minerals. Most of these secondary minerals which obliterate the classical gossan features are formed during gossan formation and therefore, they incorporate some of the released elements, becoming an important goal for the geochemistry evaluation of gossans. This may be exemplified by the alunite-garosite series which can contain high concentrations of pathfinders and target elements. It is for such samples and cases, that multi-element geochemistry has proven to be a successful tool in distinguishing gossans from common ironstones. The geochemistry evaluation of gossans is normally conducted on any ironstone suspected to be a base metals gossan; for each case, attention should be focussed on the:

(1) areal geochemistry zonation, considering that primary halo and secondary dispersion are both responsible for a zonation of suitable elements to be identified in the exploration for that specific target element in gossan. At this stage, the selection of the elements to be used in gossan identification is of considerable importance; this selection should be based on the knowledge of the host rock and the expected mineralization. Table 6.1 (Taylor and Thornber, 1992), summarizes the several geological contexts, targets and pathfinder elements to be identified in base metal gossans.

(2) Relative concentration ranges of target and pathfinder elements. Most of the elements used in gossan geochemistry have a known range in the depletion zone of the profile according to their mobility and the secondary minerals they form or they are hosted in. Any abnormal concentration of such target or pathfinder elements could be related to the source. Some other

elements are brought about by sulphide solutions; their concentrations can be used to infer the content of these primary sulphides in target base metals.

(3) Correlation between several elements analysed. This allows the identification of those elements which are increasing sympathetically in the gossan, which is a characteristic of the gossan, but is not a common feature in ironstone or ferricrite. Thus, from the study of the elements distributions and their interrelations, it may be possible to identify or characterize a gossan collected from extension areas of the known mineralized area, and to decide whether it has formed because of alteration of the particular base metal bearing sulphide lode or has formed from some barren ferruginous rock units. Hence, such geochemical studies could be used as a positive tool for guiding an exploration programme within a specific area or between different areas.

(4) Use of scattergrams to compare different gossans and to define areas of true and false gossans. Severals scattergrams have been developed for Ni-Cu sulphide gossans and very little information exists about other types of gossans. Detailed studies in terms of trace elements and their correlation should be conducted in other known gossans so as to develop enough knowledge to distinguish true from false gossans via their chemistry.

6.7.1. Geochemistry Exploration For Pb-Zn Gossans

Examples of geochemistry exploration in lead-zinc gossans are given elsewhere in the literature (Andrew, 1984; Taylor and Appleyard, 1983; Taylor and Thornber 1992). The diagnostic geochemical signature for these gossans is the high Pb-Zn-Mn-Ag content. In the highly reactive carbonate gangue Mn, Ag, Zn, Cd and Pb are all retained in gossan at high concentration.

The identification of secondary minerals such as barite, adularia, plumbogarosite and plumbogummite is important because they will give indications on the nature of sulphide mineralization and the content of lead in the primary sulphides (note that, depending on the environmetal conditions, cerussite and anglesite can appear in trace amounts). In distinguishing base metal from pyrite-derived gossan and ferricrites, however, Pb is extremely efficient (Andrew, 1984). Normally the distribution of Pb is related to the mineralized lode. Cox and Curtins (1977) studying the Lady Loretta deposit in Australia mentioned a very small lateral dispersion of lead, making it a suitable indicator for these mineralizations. Evidences of Zn

can be found in barite; this Ba-Zn association in the gossans, occurring when barite is of secondary origin (Taylor and Appleyard, 1983) suggest that during the barite formation Zn was incorporated in its structure. Zinc is also adsorbed by other secondary minerals and in most cases does not correlate with either Ba or Pb (Fig. 6.9). This element is also found widespread in large areas and it shows considerable movement vertically down profile (Cox and Curtins, 1977). It is suggested that because of the erratic distribution and high mobility of zinc, it can not be used as a reliable pathfinder or indicator of Zn-Pb-Ag mineralization using gossan sampling. Looking at the Fig. 6.9, it can be seen that zinc anomaly, although high (15%), is displaced from the mineralized lode.

Barium derived from barite, is a powerful univariant discriminant of gossan and ironstone within and between known provinces. Lead-zinc gossans of Dugald River in Queensland and those of Rosh Pinah are distinctive in their high Ba contents (Taylor and Appleyard, 1983; Andrew, 1984). In association with Pb, Ba was considered an important discriminant for base metal gossans in Southern Africa. A scattergram of Pb vs Ba developed for the Southern Africa gossans (Andrew, 1984), was applied also for Cu-Zn gossans and was successful in separating gossans from Cu-Zn mines and the sub-economic Cu-Zn gossans. The latter were collectively and very distinctly separated from pyritic gossans and laterites. With known groups of gossans in a scattergram, unknown gossans can be tested, although the use of only two variables is a disadvantage. Multi-element geochemistry should be developed for this class of gossans; in this methodology, known gossans should be used to find out the behaviour of the main base metals as to transfer this information to unknown gossans.

6.7.2. Geochemical Exploration For Cu-Zn Gossans

Diagnostic geochemical signature is defined by high Cu-Zn, Ba-Au-Ag/low Mn association. In the Southern Africa copper-zinc gossans, diagnostic features include high Cu-Pb-Ba/low Mn-Ni-Co-Cr (Andrew, 1980).

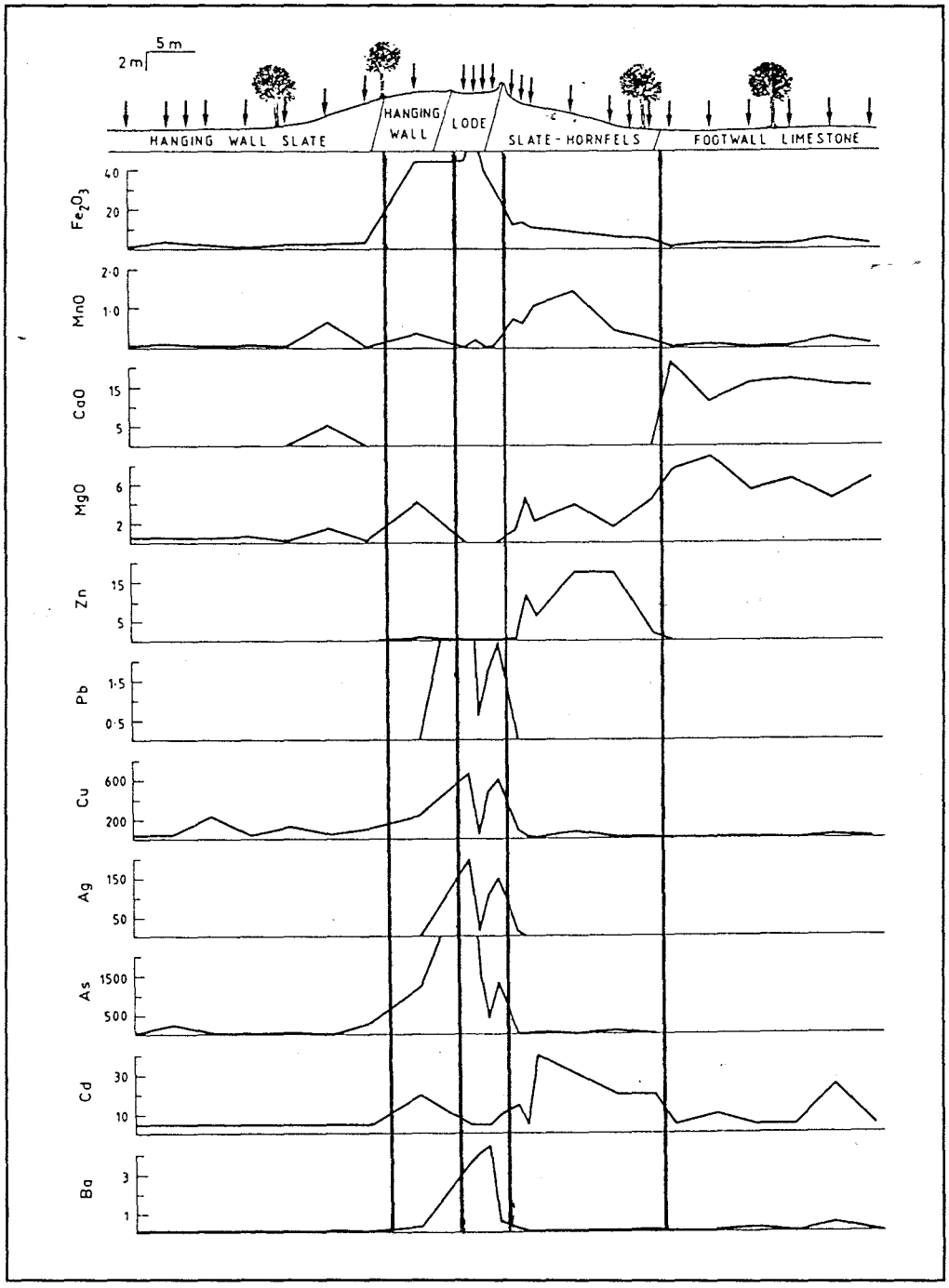

Fig. 6.9: Geochemistry profile of a lead-zinc gossan at Dugald River, NW Queensland (from Taylor and Scott, 1983). Arrows indicate sampling points.

Primary minerals for these gossans are mainly chalcopyrite and sphalerite. In sulphides dominated by these minerals, acid leaching is not as severe; thus, high concentration of trace elements in the equivant gossan, which is dominated by copper secondary minerals, will be

common (Table 6.4). This was the case in Gorob and Ongeama in Namibia, where Co, Ni, Zn and Pb were considered retained (Andew, 1980). At the Letaba Zn-Cu prospect, Cu, Zn, Co and Cd are highly anomalous in gossans due to the moderate leaching. These elements together with the oxidate minerals may elucidate the nature of the gossan, as false or true. According to Andrew (1984), Ba and Pb can both form discrete oxide minerals with Mn, while Co, Ni and Zn may form significant associations with Mn. This association does not reflect any feature of the primary sulphide, but it makes Mn important in geochemical sampling, as it can yield significant amounts of these base metals, according to the content in the precursor sulphides.

Where copper is the only mineralization, such as in porphyry copper, the mineralogy is dominantly chalcopyrite and bornite with minor amounts of molybdenite, sphalerite and pyrite. Supergene enrichment sulphides include chalcocite, covelite and minor amounts of bornite; at the oxidized zone there are malachite, azurite, cuprite and crysocolla (Schwartz, 1966). Anderson (1966) has summarized the capping interpretation procedures in Cu-gossans; common caps may include: goethite, jarosite, hematite, antlerite-brochantite and malachite caps.

Grade prediction for each of these cappings utilizes empirical correlation of the primary grade and chalcocite enrichment grade of the sulphide zone with the following:

- Percent goethite in the hematite.
- Percent hematite in the limonite.
- Percent jarosite in the limonite.
- Diagnostic copper minerals.
- Residual copper content of the capping.

Table 6.4: Mineralogy and distinctive oxidate minerals of selected Cu-Zn gossans, Southern Africa (extracted from Andrew, 1980).

Locality	gossan type	age and depth of weathering (m)	Fe-oxides	oxidate minerals
Otjihase	pyrite-calcopyrite-quartzite; pyrite-qzite	Cretaceous 20-25	goethite; hematite; jarosite	malachite; plumbogummite
Matchless	chalcopyrite-pyrite jasperoid chalcopyrite- chlorite schist	Cretaceous 15-25	goethite; hematite; jarosite	malachite; crysocolla; brochantite; plumbogummite; plumbojarosite
Gorob	chalcopyrite-jasperoi pyrite-sericite-quartzite	Eocene 30	goethite; hematite	crysocolla; malachite; paratacamite
Ongeama	po-py-qtzite qz-mt-ba-sr	Miocene 15-20	goethite; hematite	

6.7.3. Geochemistry Exploration For Ni-Cu Gossans

Ni-Cu sulphide mineralizations are common in greenstone belts , where they are associated exclusively with the ultramafic phases, consisting of serpentinites and Komatiites. Typically the mineralization consists of a pyrrhotite-pentlandite-pyrite-chalcopyrite assemblage. Where such rocks undergo a deep weathering process, gossans may be developed. The discovery and recognition of true nickel gossans is not only hampered by the lack of outcrops in these deeply weathered terrains but also, to at large extent, by the wide variety of other types of ironstone. Nickel-copper false gossans superficially resemble true gossans and include gossanous material derived from non-economic sulphides, typically pyrite and laterite. Ni-sulphide gossans are indicated by relatively high Ni and Cu; low Mn and Cr; very low Pb, Zn and Mo. These Ni-Cu gossans are also invariably enriched in Pt, Pd and Se (Clema and Stevens-Hoare, 1973; Moeskops, 1977).

A study by Cochrane (1973) in Moeskops (1977) in Yilgarn (Australia), has revealed more

details to be taken into account in geochemical exploration for Ni-Cu gossans:

(1) Unlateritized true Ni-Cu gossans generally yield high Cu (500-5000 ppm) and Ni (1000-5000 ppm) associated with low $Cr^{(S)1}$ (500 ppm), Mn (500 pmm) and Zn (100 ppm).

(2) False gossans, derived by non-lateritic weathering of unmineralized ultramafic rocks, generally yield similar, or lower, Ni values to those observed in true gossans but are strongly depleted in Cu (100 ppm). Lateritic variants are commonly enriched in $Cr^{(s)}$ (2000-10000 ppm) and Zn (250 ppm).

(3) Lateritic false gossans derived from various rock types are characterized by variable Mn (20-1200 ppm), Ni (15-3500 ppm), $Cr^{(s)}$ (30-10000 ppm) and Zn (20-500 ppm).

In addition, true gossans are characterized by Ni/Cu ratios lower than 10 (mostly 2-6; 5-20 in false gossans) .

Clema and Stevens-Hoare (1973) derived a successful empirical scattergram (Fig. 6.10a), which makes use of various combinations and ratios of the most common elements occurring in Ni-Sulphide gossans (Cu, Ni, Zn, Mn and $Cr^{(s)}$), to distinguish true and false gossans. Joyce and Clema (1974) in Moeskosps (1977) applied the statistical technique of principal component analysis to develope a simple scattergram based only on Cu, Ni and $Cr^{(s)}$ values. As in Fig. 6.10b, this scattergram can also differentiate false and true gossans.

The true and false gossans can also be distinguished fairly well using a triangular plot with Cu-Ni-Zn. This diagram, according to Moeskops (1977) is generally about 80-90% successful in distinguishing true and false gossans (Fig. 6.11). Exploration procedures should include collection of gossan samples so as to analyse the pathfinders and target elements and, using these diagrams, find out if the gossans are likely to be related to an economic sulphide deposits or are simply an oxidation of pyrite rich ironstone.

One of the most important tasks of geochemistry in gossan evaluation is to assess the approximate composition of the primary sulphides. For this purpose, Ir, Pd and Pt have been identified as immobile elements which are concentrated at the weathering zone. Taking into account their affinity for nickel and copper, many workers have admitted that a proportion can be derived from these elements with the base metals content of the original sulphides (Keays and Devison , 1976; Traves et al., 1976). From the Fig. 6.12 it can be seen that even in highly

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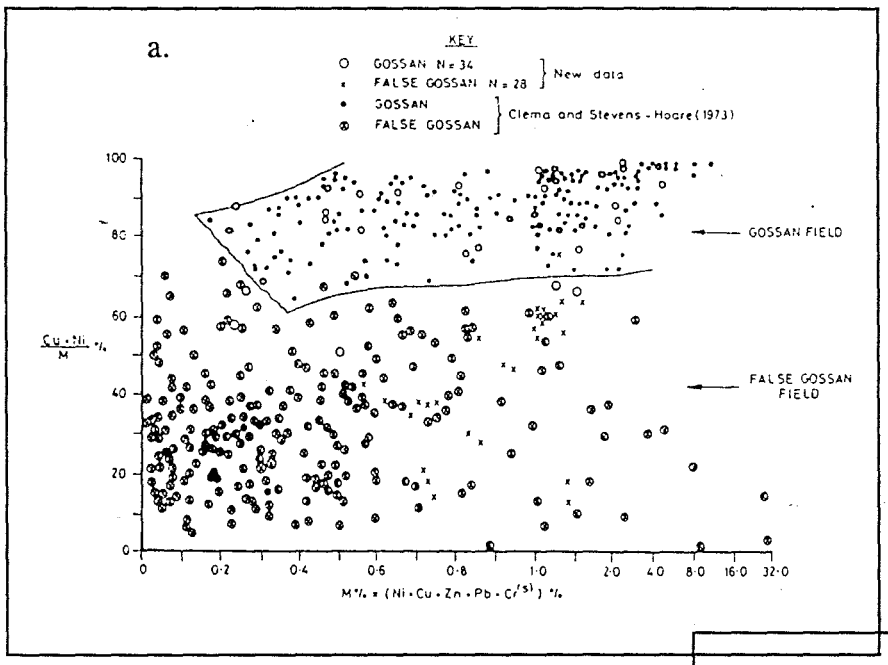
[1] perchloric-nitric acid-soluble chromium

leached gossan, Pd and Ir are maintained at abnormal levels and are consistent with the high Ni content of that horizon.



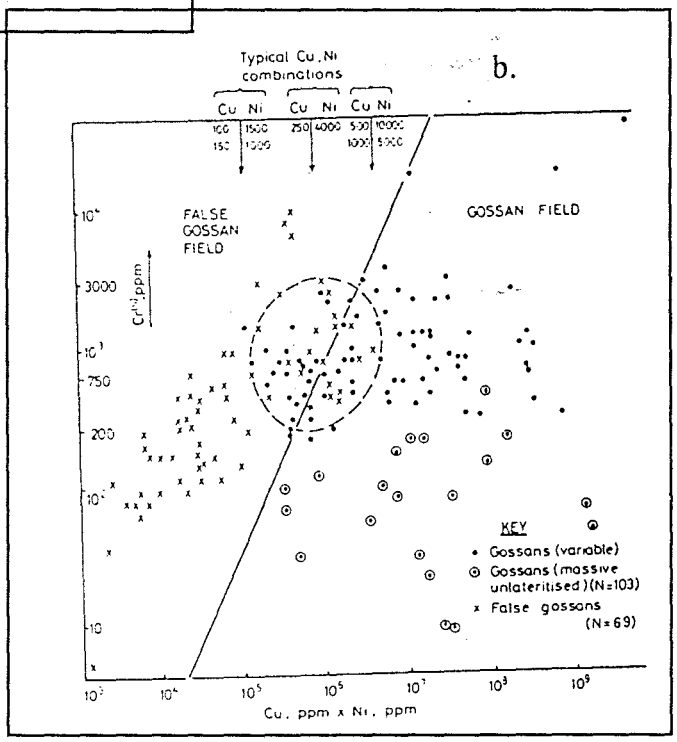


Fig. 6.10: Gossan scattergrams designed to distinguish true from false massive nickel sulphide gossan (a. by Joice and Clema, 1974 in Moeskops, 1977 and b. from Clema and Stevens-Hoare ,1973).

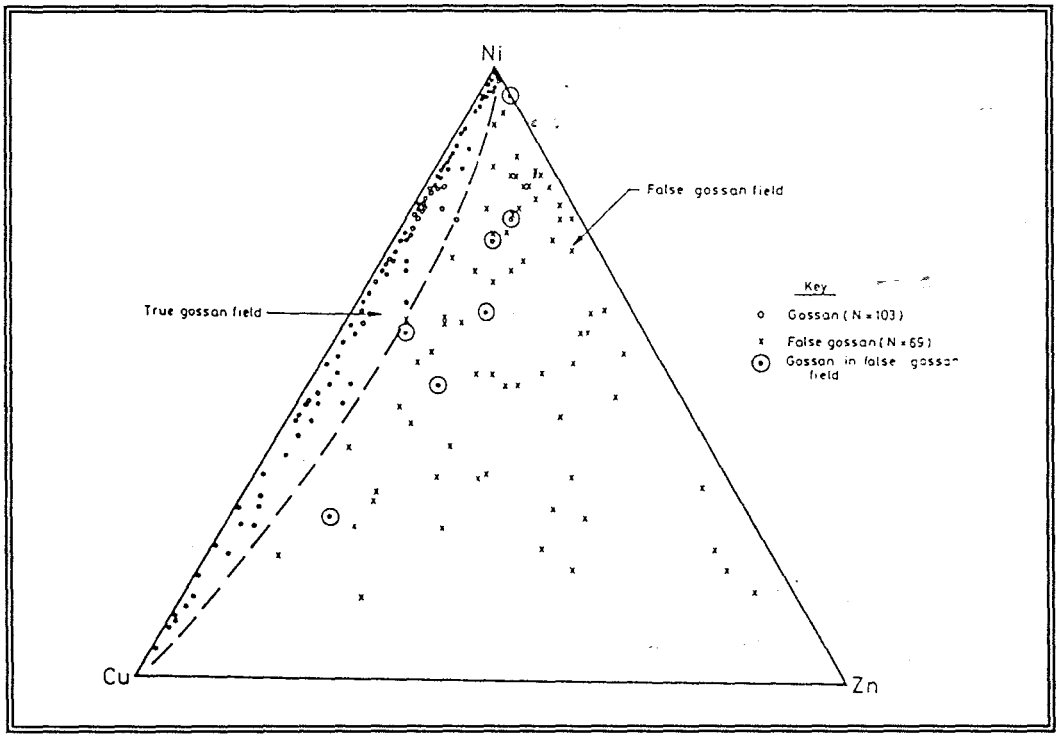


Fig. 6.11: Triangular diagram based on weight Ni, Zn and Cu, showing assigned true and false gossan fields, by Moeskops (1977).

From this observation McGoldrick and Keays (1981) concluded that Ir is not mobile during gossan formation and the absolute Pd and Ir contents of gossan can be used to provide a reliable indication of the Ni grades in the precursor sulphide assemblage, after due allowance for Ir enrichment has been done. The same exercise is possible using Pt because this also becomes concentrated.

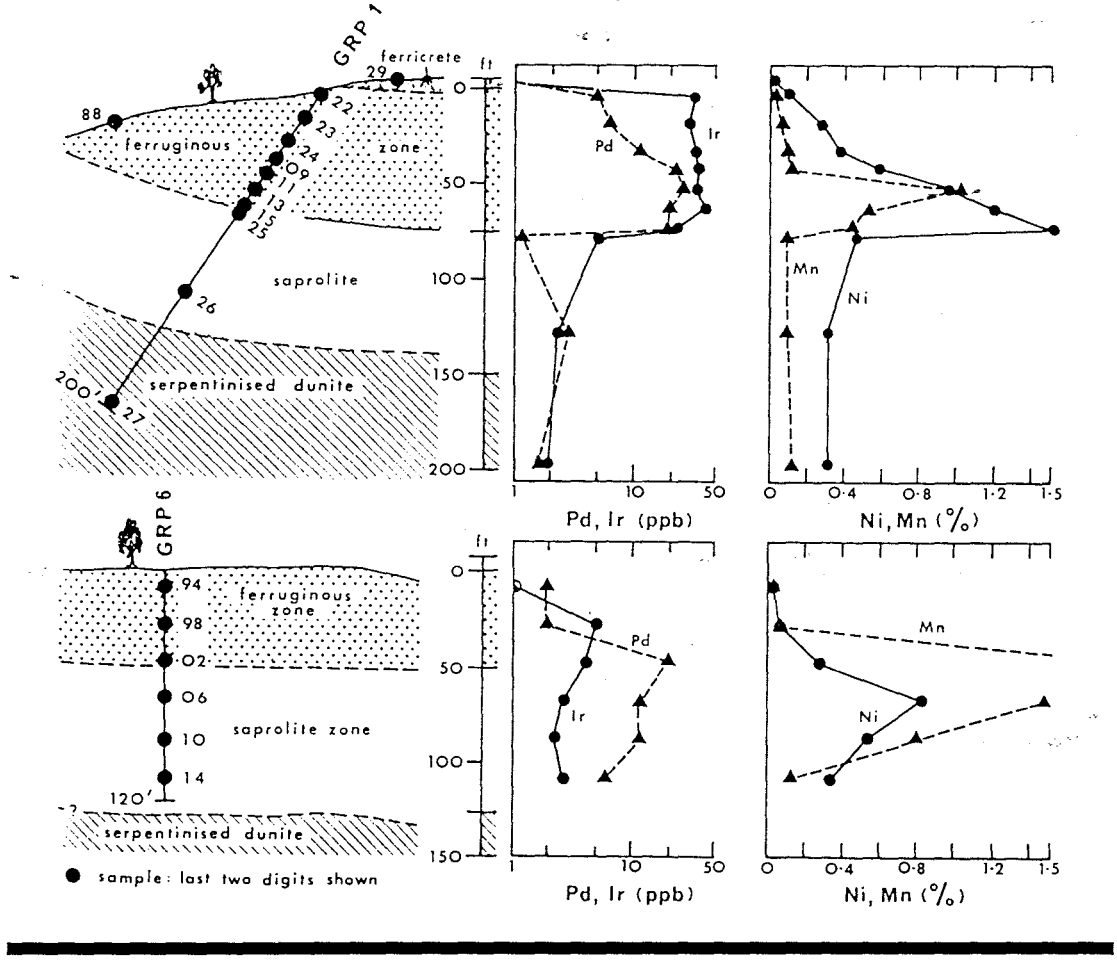


Fig. 6.12: Profiles showing the retention of Pd and Ir and their consistence with Ni anomaly (from McGoldrick and Keays, 1981).

7. LATERITES

7.1. DEFINITION

Laterite originally was the name given to a single zone in a soil profile by Buchman in 1807 (Hortz, 1964) for a reddish-brown ferruginous residual rock in southern India, which hardens on exposure and was used for building. Subsequently the term was widely used for many red, ferruginous weathering products in tropical regions.

Other scientists (Maignien, 1966 and Millot, 1964 in Nahon and Tardy, 1992), have proposed that the term laterite should be extended to all weathering products that have those chemical and mineralogical characteristics specific to tropical environments, rather than be restricted to those that are hard or potentially hard. In this sense, the term includes materials commonly associated with indurated ferricretes such as red or yellow ferralitic soils, tropical ferruginous soils, kaolinitic saprolites and lithomarges, all of which are soft and cannot harden (Nahon and Tardy, 1992). Lateritization is a specific weathering process of tropical and equatorial terrains, is observed in more than 30% of the emerged earth (Pedro, 1966 in Lecomte, 1988). True laterites with their duricrust horizon commonly occur in seasonal savanna-type tropical regions.

7.2. LATERITIC PROFILE

Lateritic profiles are common in tropical environments. Such soils are mainly typified by five horizons, which could be described as follows, from bottom: Fresh rock; transition zone; pallid zone or saprolite; mottled zone; pisolitic layer or cuirasse and true soil (Smith and Pedrix, 1983; Lecomte, 1988; Mann and Webster, 1990; Nahon and Tardy, 1992).

(1) Transition zone: this is the lowest part of the weathering profile overlying fresh rock; it presents the rock texture well preserved.

(2) Saprolite: can be 25 to 60 m thick, with the thickness tending to be greater on the felsic volcano-sedimentary and granitic rocks and less on the basic rocks. The main structure of the bedrock may easily be recognised. The texture is sandy and the grain size fraction between 63 and 500 micrometres; residual mineral grains can be recognised such as micas; the degree of weathering increases upwards and in this sense, the persistence of the primary textures

gradually reduces. The mineralogy of this horizon is dominated by authigenic minerals such as kaolinite and smectite. These minerals are crucial in base metals behaviour in a lateritic profile. Less important are resistant minerals including rutile, zircon and amphiboles.

(3) Mottled zone: the top half metre of the saprolite is commonly a mottled zone in which vermicular, nodular and concretionary iron enrichment are set in a clay-rich matrix. Cemented-sized pisolites are present in the top of the mottled zone but each pisolite is isolated by the matrix. The mottled zone coincides with the present day water-table (Mann and Webster, 1990). No relict rock fabrics or structures are preserved in this horizon.

(4) Iron crust or cuirasse: It follows after the previous horizon in gradational transition. The thickness is variable and sometimes can reach 5 m. It develops where the purple-red hematitic nodules that form in the mottled zone (Nahon et al., 1980) become more numerous, finally coalescing into an indurated cuirasse or ferricrite. Nahon and Tardy (1992) divided the iron crust into:

(i) Soft, nodular iron crust;
(ii) Indurated, conglomeratic iron crust;
(iii) Pisolitic iron crust;
(iv) Pebbly ferruginous layer.

The mineralogy consists essentially of goethite, hematite forming nodules and pisolites. The ferruginous nodules are well rounded and small, no larger than 1 cm in diameter; with or without a thin, bright cortex. The nodules without cortex are elongated and usually display an internal lithorelict structure. Other minerals are gibbsite, quartz and kaolinite.

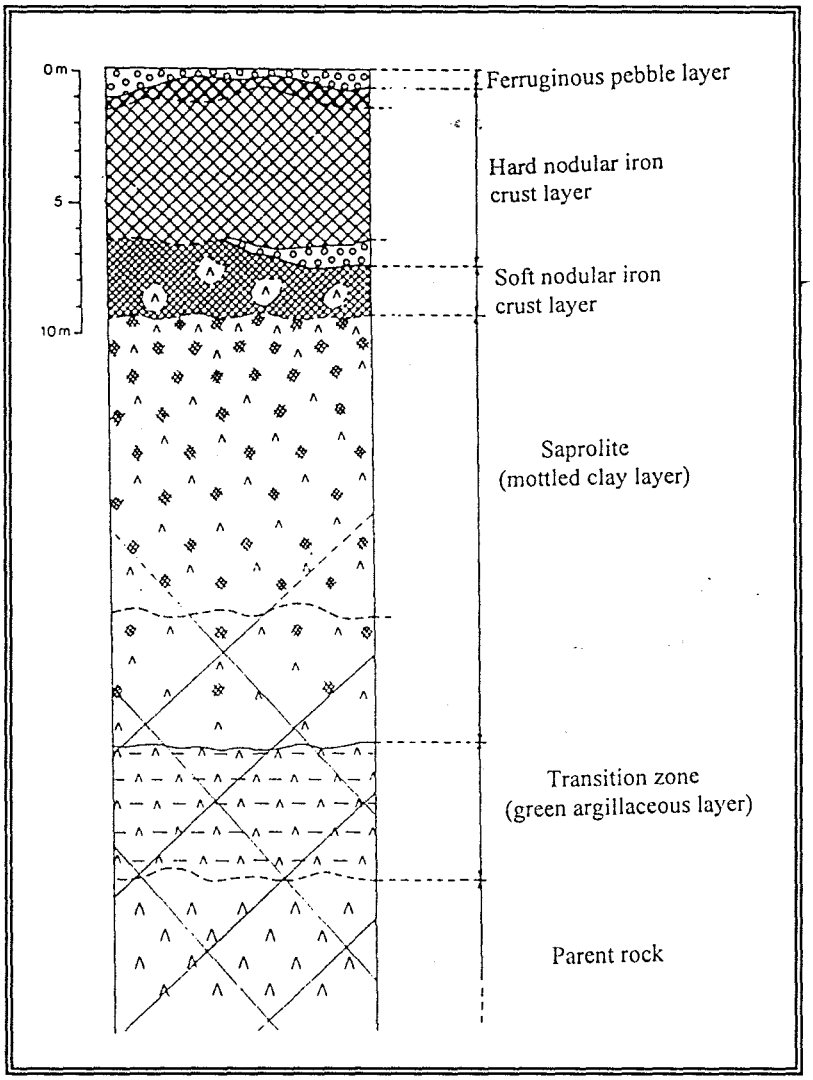


Fig. 7.1: Typical lateritic profile (modified, from Ambrosi and Nahon, 1986).

7.3. PROCESS OF NODULES FORMATION

The process of nodule formation was discussed by Nahon et al. (1980); Tardy and Nahon (1985). According to these authors, the formation of ferruginous pisolites which extend to all tropical environments corresponds to a lateritic alteration of sedimentary, metamorphic and igneous rocks, and thus, is a pedogenic process. Pisolites are formed by successive centripetal concentration and reorganization of iron oxides and hydroxides.

One of the most remarkable facts in the process of a ferricrete formation is that iron is leached from large size pores and accumulated in small size pores, which means that it moves from sandy to clay texture. This process starts to occur above the water-table and is continuous

until the true soil. The minerals are formed in situ above the water-table, where mottles begin to form and the first mineral to form is goethite. Farther upwards, hematite follows goethite, and nodules develop from mottles (Fig. 7.2). In both cases, iron moves from the outer part to the inner part of the concretion. The driving force of this migration and accumulation seems to be the initial difference in the size of the pores, which tends to be accentuated as the concretion develops. These centripetal rearrangements, as can be seen in Fig. 7.2, begin at the discontinuity which exists or remains in the lower part of the weathering profile.

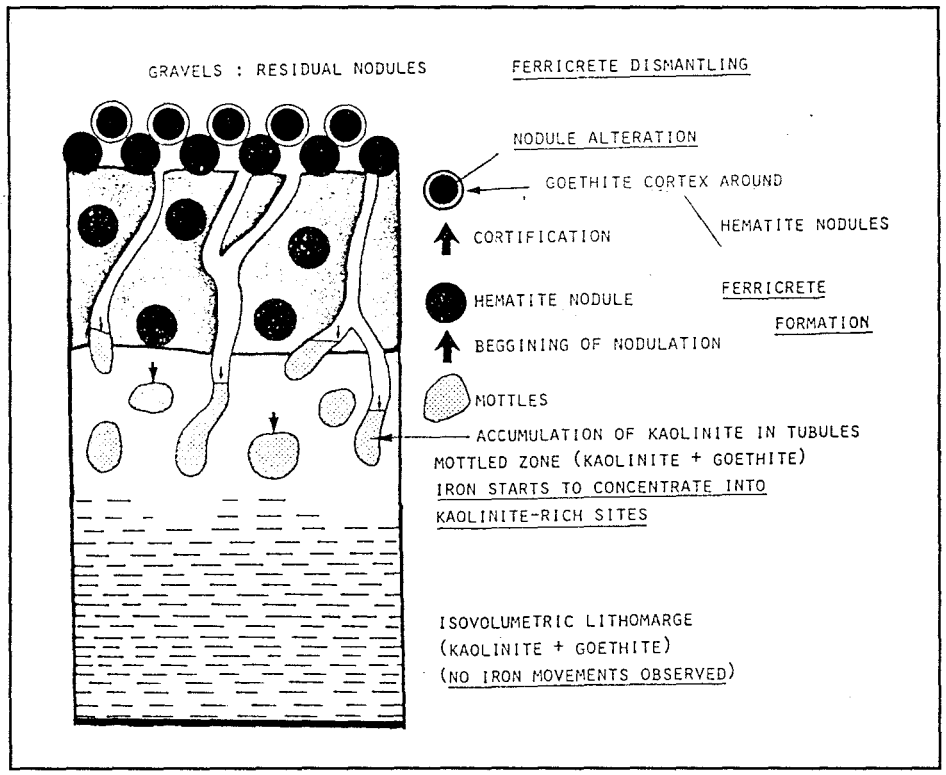


Fig. 7.2: Schematic representation of the process of pisolite formation (modified, after Nahon et al ., 1980).

Nahon et al. (1980) have stated that the fact that the laterites are characterized by pisolites with greatly variable sizes, internally complex, reciprocally interfering, strongly deformed and set in a fine hematitic argillaceous matrix means that they are in situ features. Initially these segregations are smaller, less regular and commonly coated with manganese (Mcfarlane, 1983). The base of the pedogenic packed pisolitic laterite is often platy, with horizontal cavities heavily coated with blue-black manganese.

7.4. DISPERSION MODELS AND DISTRIBUTION OF BASE METALS IN LATERITIC PROFILES

In deeply weathered terrain where lateritic profiles are developed, three dispersion models are possible (Zeegers and Lecomte, 1992):

(a) The lateritic profile is mostly preserved, so that the ferruginous cap is outcropping or suboutcropping (A model).

(b) The pre-existing profile is truncated as the result of erosion, thus, the hard cap is no longer preserved (B model).

(c) The pre-existing lateritic profile has been entirely eroded, and soil profiles are the product of weathering under more recent climates (C model). When erosion is intense, the bedrock may even outcrop, resulting in a situation where the primary halo might be sought using lithogeochemical methods. This model does not present most of the lateritic features, therefore, will not be discussed here.

The models described above can apply in seasonally humid terrains (Savannas) or in humid tropical terrains (Rainforests).

7.5. LATERITIC PROFILES IN SEASONALLY HUMID TERRAINS (SAVANNAS)

These lateritic soils may be found occupying a wide belt bordering the equatorial zone, including the Brazilian shield, West and East Africa, parts of India and Northern Australia. The annual rainfall in these areas ranges between 600 and 1500 mm.

The profiles, if preserved, exhibit the hard carapace (Fig. 7.1) and if truncated they possibly present nodules and a stone line which is recognised as the contact between the bottom lateritic profile and the upper recent soil (Fig. 7.8).

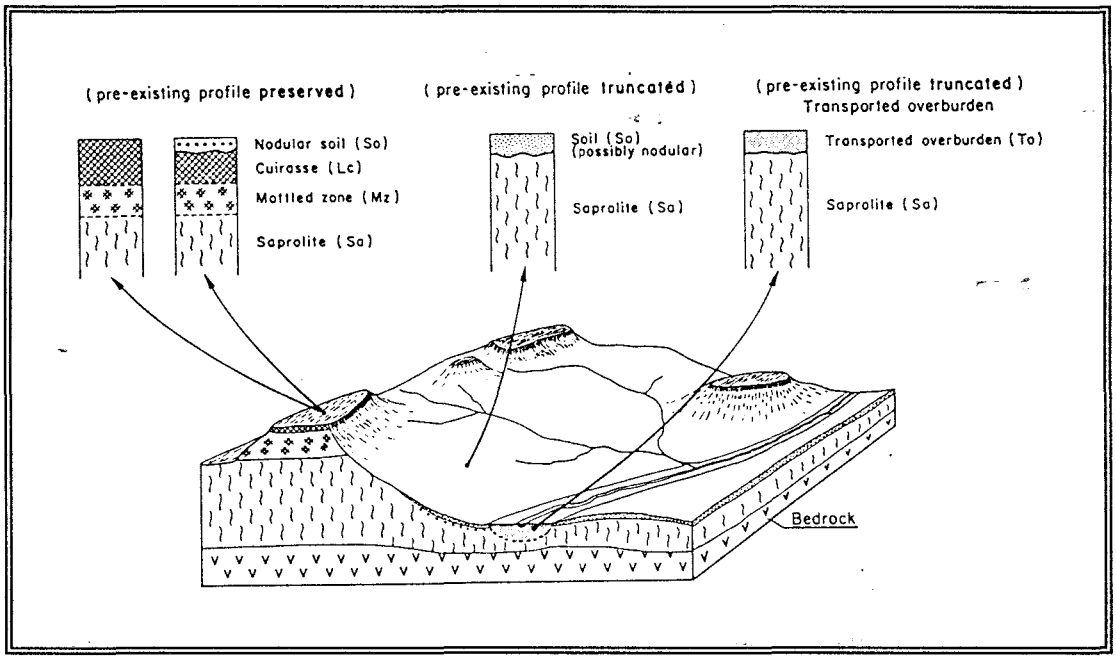


Fig. 7.3: Diagram showing the general landscape and the weathering profiles related to preserved or truncated lateritic profiles in Savannas (from Zeegers and Lecomte, 1992).

7.5.1. A-type Dispersion Model: Pre-existing Profile Mostly Preserved

Several studies have been carried out aiming to identify the horizon where base metals are concentrated and to identify the factors determining their concentration at that depth. Table 7.1 below gives the concentration of base metals in a lateritic profile developed over basic and ultrabasic rocks (Zeissink, 1969).

This profile suggests that Nickel is concentrated at the upper zone of the lateritic profile up to a depth of about 10 metres and then drops down; this is the behaviour also of Fe_2O_3 values. No zone of the Ni concentration is present near fresh serpentine-weathering zone interface.

Magnesium rich minerals, which are concentrated in the base of the profile, can offer potential sites for Ni substitution. Zeissink (1969) defined two groups of Ni laterites: those with high MgO contents and low iron oxides, a group in which the Ni enrichment occurs in the base of the profile, in the saprolite; and those with low MgO and high iron oxides content, a group for which Ni will be found in the pisolitic layer. The profile in Table 7.1 belongs to the second group. Zeegers (1979) stressed a good correlation between either Ni and Cu with iron

Table 7.1: Concentration of base metals in a lateritic profile, in ppm, (extracted from Zeissink, 1969).

Depth (m)	Pb	Zn	Cu	Ni	Co	Mn
0.8	18	270	200	17800	4290	8800
1.7	18	268	180	18000	4620	9130
3.8	16	321	88	19800	4620	4730
5.3	18	276	90	11900	1540	3410
6.8	18	303	55	22500	3960	4730
8.38	16	427	43	19800	2750	2530
9.91	25	349	39	16600	1430	2310
11.43	18	123	46	9500	900	2090
12.96	18	77	13	5100	340	970

oxides (correlation coefficient of 0.5 for both). Cobalt and nickel exhibit the same radii and normally they behave similarly. However, in Table 7.1 cobalt is shown to be strongly concentrated at the upper part of the profile.

Lead presents remarkably constant values along the profile; the same behaviour was described by Zeegers (1979) who classified Pb as an element unaffected by ferralitic weathering; this base metal shows no association at all with iron oxides or any preference in a lateritic profile.

Copper, which could be expected to be depleted because of its high solubility in this environment, is highly concentrated, up to 30 fold. Besides the organic matter which could be very important at the superficial horizon, the weakise scavenger property of oxides over this base-metal is apparent in the reduction of its content at the depth where Ni, Co and Zn reach their maximum.

Zinc in the lateritic profile exhibits its high mobility character, so that it is difficult to use this base-metal as an important indicator for mineralized bedrock.

Smith (1977) found a very similar association between Ni, Co and Cu with both goethite and hematite in unmineralized lateritic profile (Fig. 7.4). Its work has shown that during

lateritization of ultrabasic rocks, Ni is firstly associated with smectite, while Cu is associated with goethite. With further weathering, an association of Ni with goethite occurs, whereas that of the Cu and goethite continues. At a later stage, as the iron oxide crystals grow in size, the concentration of some elements that were previously associated with iron oxides, such as Ni and Cu, is reduced to low levels. This tendency towards the reduction of base metals in the pisolitic zone as the iron content increases was also identified by Zeegers and Lecomte (1992). The later authors divided the base metals into two groups:

(I) elements such as Cu, Zn, Ni, Co, are associated with Kaolinite, smectite or other secondary minerals forming the saprolite, in this connection, Ni normally appears in garnierite, in the base of the profile. These base metals are strongly leached when the Fe_2O_3 contents increase.

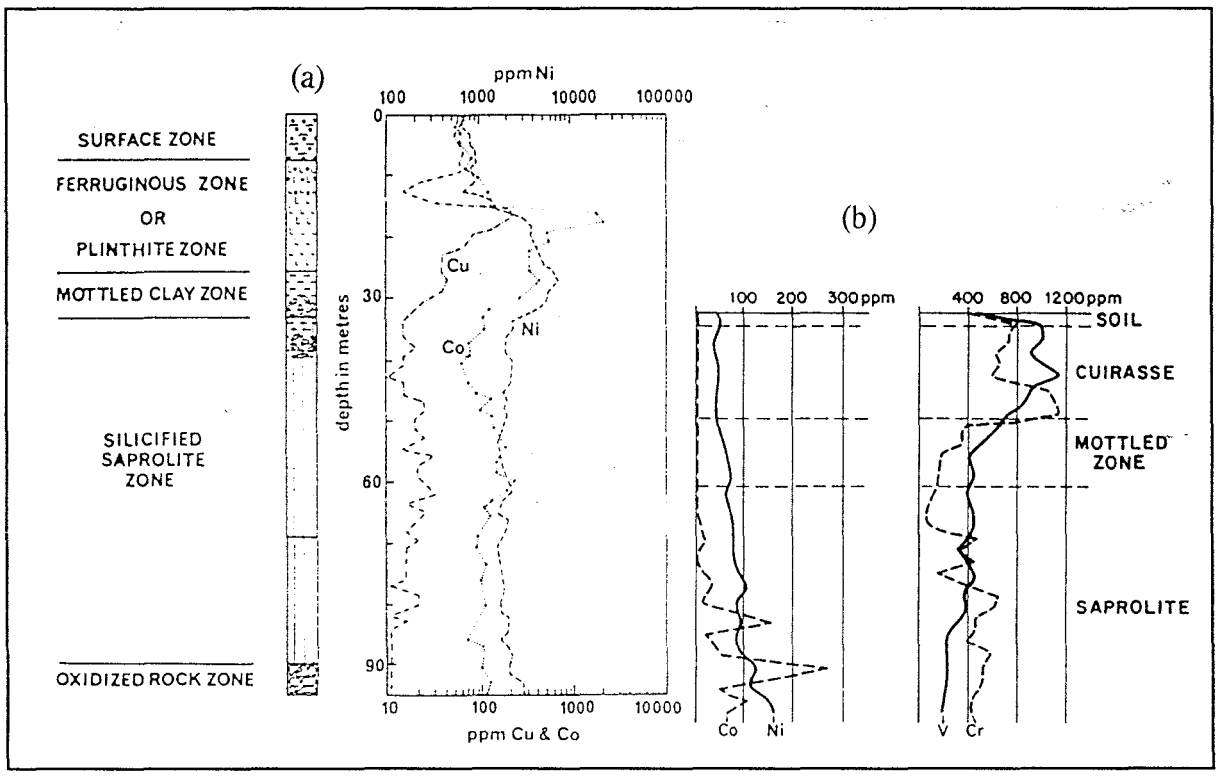


Fig. 7.4: Average variations of selected base metals in two lateritic profiles: (a) unmineralized laterite profile, Western Australia, Smith (1977); (b) lateritic weathering profile of Burkina Faso, Zeegers and Lecomte (1992).

(II) elements such as Mo, which have strong affinity for iron oxides. These will be enriched in the Fe-rich horizon.

The behaviour of molybdenum in lateritic profile was studied by Tooms et al. (1965), using the Sierra Leone example. From the diagram in Fig. 7.5, it can be seen that in residual lateritic soil, the mineralization can be well depicted by soil sampling. According to Tooms et al. (1965), dispersed Mo tends to be concentrated in the horizon of iron oxides accumulation; this is due to the possible fixation of Mo by sorption on to freshly precipitated iron oxides or by co-precipitation with iron oxides.

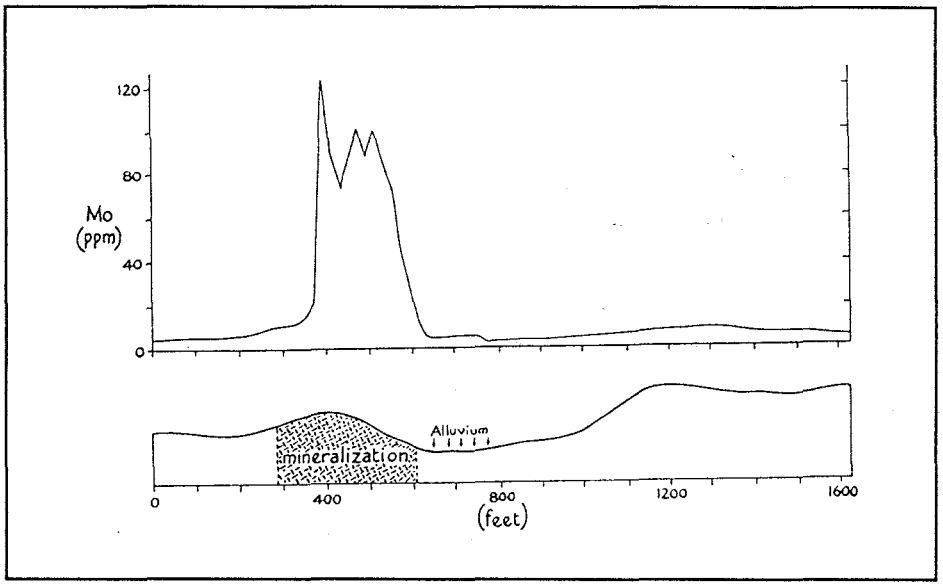


Fig. 7.5: Molybdenum distribution in residual soil overlying a mineralization (from Tooms et al., 1965).

In deeply weathered terrains where strong leaching occurs, base metals may be removed from the environment reducing the contrast; thus, even small contrasts could be significant. If the profiles are complete, the Fe oxides are the key minerals at the upper part of the profile; but even in this horizon with strong leaching and increase of the Fe_2O_3 content, only Mo still depicts the bedrock. Ni, Cu and Co appear as residuals in the base of the lateritic profiles incorporated in kaolinite, smectite or forming proper secondary minerals.

7.5.2. Implications For Base Metals Exploration In A-type Model

In the light of the behaviour of the base metals described above, it is worth while to define which target and pathfinder elements to consider and in which horizon sampling should be

carried out in a lateritic profile, so as to have the highest contrast possible.

High Ni in the pisolitic zone is not a reliable indicator of the presence of mineralization in laterite (Smith, 1977; Fig. 7.4a). Ni is rapidly depleted with the onset of lateritic weathering and it can also concentrate to high values in clay derived from rocks which are barren of mineralization. Samples taken from the saprolite may give reasonable indication of the degree of accumulation of Ni in kaolinite, smectite or garnierite and this can depict the character of the bedrock, Fig.7.4b.

Copper has low mobility in the mottles and pisolitic zones because of its association with iron oxides. The dimensions of any secondary Cu halo around mineralization are usually limited. Cu anomalous values (> 100 ppm) should be checked to see the areal distribution. These values become significant when they are fairly consistent with depth and continue below the mottled zone.

Cobalt has a very similar chemistry to Ni; thus, the ratio Ni/Co is fairly constant both in fresh rock and in deeply weathered profiles. This ratio is usually between 10:1 and 30:1 in barren environments and 20:1 to 50:1 in mineralized associations. In Mn-rich environments this may change (Smith, 1977).

Lead content in lateritic profiles is fairly consistent in the profile and mostly consistent with that of the fresh rock.

Molybdenum normally appears enriched in the pisolitic horizon because of its association with iron oxides and co-precipitation with those oxides; further leaching by hydromorphic processes may be possible.

Where the lateritic profile is complete, the dispersion mostly proceeds from the combination of hydromorphic and detrital processes, both past and present, related to the formation and evolution of the lateritic profile. Samples can be collected either at the pisolitic horizon or at the saprolite. In comparison with that of the bedrock, the concentrations of the base metals in the lateritic profile vary according to each element; this is a function of the affinities either with goethite/hematite or with kaolinite/smectite; the following is the relative concentration of the concerned base metals (Tooms et al., 1961; Zeegers, 1979; Zeegers and Lecomte, 1992).

In the pisolitic zone:

- Pb is similar to that of the bedrock.

- Cu, Zn are depleted in relation with that of the bedrock.
- Mo is enriched in this horizon.

In the saprolite:

- Many of the target base metals are not strongly leached and anomalies are mostly residual; this is the case for Cu, Pb, Co and Ni. Zn appears to be strongly dispersed by hydromorphic processes.

7.5.3. B-type Dispersion Model: Pre-existent Profile Truncated

B-type dispersion model is based on the absence of the hard cuirasse horizon. The pre-existing profile has been eroded to a lower level either to the mottled zone or to the saprolite. Depending on the depth of the truncation, relicts of the pre-existing profile may be observed on the top of the present profile. Since the hard cuirasse has been removed, the softer underlying horizons are more easily eroded, so that lower levels of the saprolite are exposed. An example of these profiles was given by Tooms and Webb (1961) from Eastern Africa. Using this example, three principal horizons are developed in these laterites (Fig. 7.6):

The A horizon is perennially freely drained and consists of light yellow-brown to red-brown sandy loam, essentially free of rock fragments or other rubble.

The B horizon is immediately above the highest level attained by the water-table. It is composed of dark red to black nodular concretions of sesquioxides, set in a red-brown sandy loam matrix. The nodules are originally quite soft but become progressively harder as the matrix moves towards the top of the horizon. The contact with the A horizon is generally sharp and marked by a stone line. The mineralogy depends on the level of truncation; in East Africa a pisolitic zone was identified, with the characteristic high content of hematite and goethite.

The C horizon lies gradationally below the B horizon and is subjected to alternating oxidation and reduction. According to Tooms and Webb (1961), this is responsible for the ferruginous colour observed in the mottled zone. The C horizon is the highly decomposed rock (saprolite). The dominant material is kaolinite which decreases towards the base with the increase of smectite.

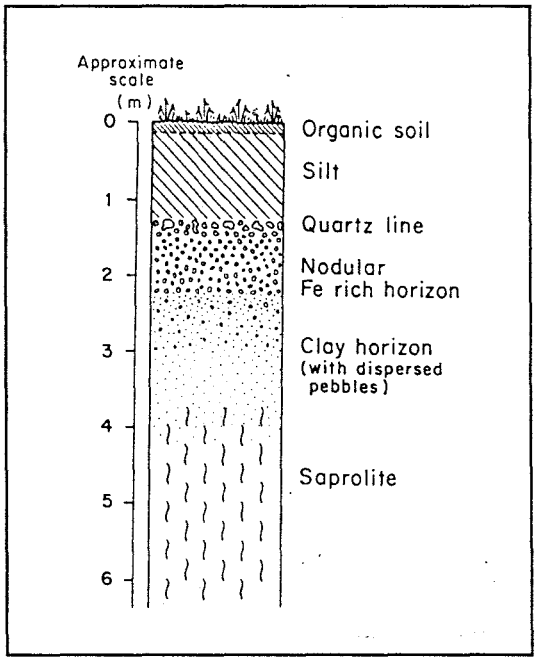


Fig. 7.6: Idealized weathering profile with a Fe-rich nodular accumulation horizon (stone line) in Eastern Africa (modified after Tooms and Webb, 1961 from Zeegers and Lecomte, 1992).

The profile described above is very similar to that described by Lecomte (1988) for Central Africa in rainforest environment (Fig. 7.8). Zeegers and Lecomte (1992) suggest that the profile in Eastern Africa could be a very early stage of the development of the stone line profiles.

The behaviour of base metals in a B-type lateritic soil profile with the special reference to Cu, Pb and Zn was studied by Tooms and Webb (1961); Goossens (1974). Figure 7.7B. shows the variation in copper anomalies in different soil horizons overlying the mineralization. From this figure it can be seen that the mineralization is reflected in the three soil horizons. The copper content of the pisolitic horizon, both in background and anomalous areas, tends to be higher than in other horizons. Although the lateral extent of the anomaly is almost the same in all horizons, it should be noted that the anomaly peak becomes progressively sharper, as it moves to the saprolite.

In Burkina Faso, which as a climate with well-contrasted seasons (Zeegers and Lecomte, 1992), the distribution of Pb, Cu and Zn in several soil profiles seems to be similar to the previous case, Fig. 7.7B. The profiles are located 0.3, 3 and 15 m of distance from the

mineralization (Goossens, 1974). Up to 3 metres, the mineralization is well depicted at the probable depth of the pisolitic horizon but at 15 metres there is no evidence of the mineralization. According to these data, the dispersion of lead is restricted, both laterally and vertically, to small envelopes less than 15 m in extent around the primary mineralization. The vertical distribution of lead shows highest concentration at the middle of the profile. The zinc anomaly, although weak, can be identified at the same depth as lead. It is considered that the zinc distribution simply reflects the dispersion associated with the lead sulphides mineralization (Goossens, 1974).

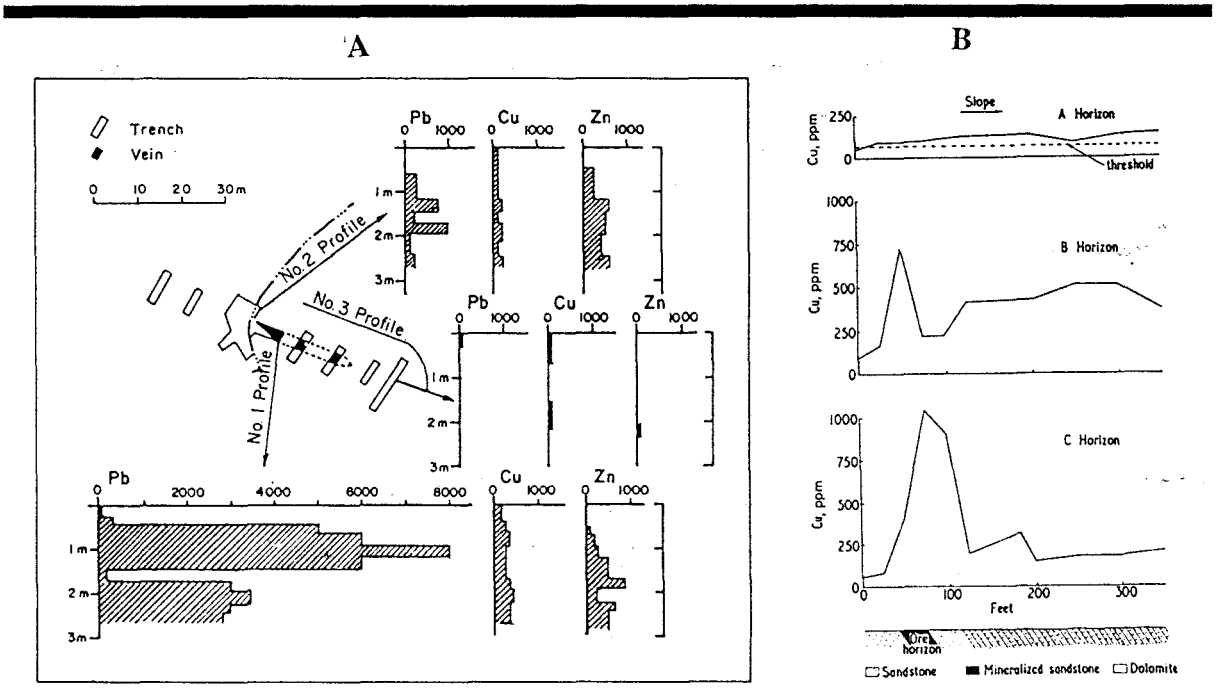


Fig. 7.7: A. Distribution of lead, copper and zinc (ppm) in trenches made at different distances from the mineralization (profile 1: 0.3 m distance; profile 2: 3 m distance; profile 3: 15 m distance), after Goossens (1974). B. Vertical distribution of copper in a laterite, East Africa. From Tooms and Webb (1961).

7.5.4. Origin of Stone Lines

Stone lines are peculiar features in truncated lateritic profiles and are found mostly in rainforest environments. Laporte (1962) in Lecomte (1988), proposed the formation of stone lines by the downward movement of coarse fragments as a consequence of pedoturbation; since then, several hypotheses have been put forward to explain the origin of that horizon of lithofragments; the most significant being Lecomte's (Lecomte, 1988). According to this author, the low pH in tropical environments causes a strong leaching of the soluble constituents of the soil; this chemical reweathering by aggressive leaching of pre-existing lateritic profiles destroys the saprolite and produces the unconsolidated clay-sand horizon. During this process, the coarse fragments accumulate by downwards migration (Moeyersons, 1978 in Lecomte, 1988). The gravitational settling of coarse fragments of different composition, and the subsequent accumulation takes place at the lower limit of water impregnation and forms the stone line, whereas leaching and homogenization occur throughout the upper water-impregnated layer. The role of termites in the homogenization of this horizon has been recognised by several authors (Lecomte and Zeegers, 1992). According to this hypothesis, the contact between the true soil and the accumulation horizon represents an impregnation front and the lower limit of the intensively leached environment. This interpretation of stone lines is consistent with the composition of the material found in it and can be understood as being concordant with the pisolite formation from the water-table upwards (Nahon et al., 1980). Both materials constitute the stone line and since they are recognised as residual, near surface sampling procedures can be used effectively and the results understood as depicting the rock underneath.

It could be understood that not all stone lines have this origin; some are clearly sedimentary, having exotic, perhaps rounded, clasts of distant provenance and in this case the surface soil will not be residual.

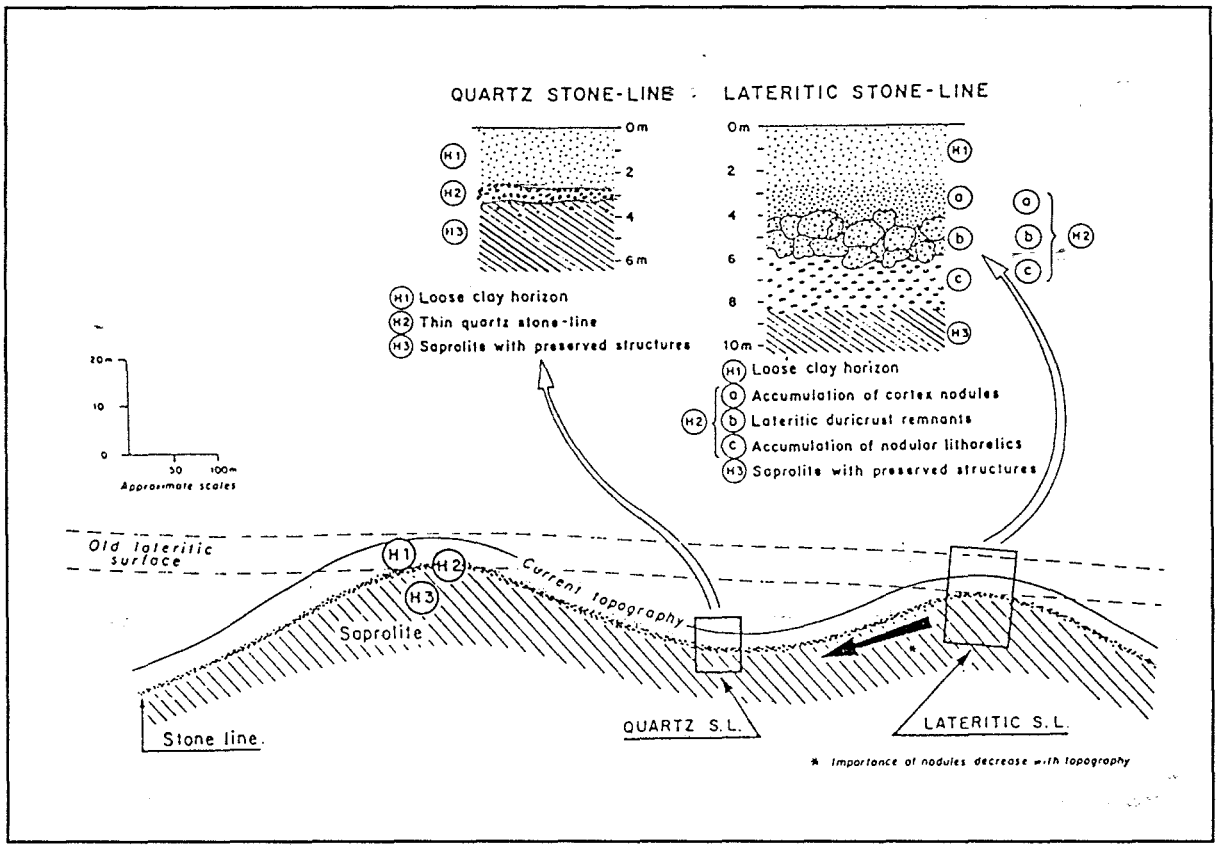


Fig. 7.8: The two end-member types of stone lines, according to Lecomte (1988).

7.5.5. Implications For Base Metals Exploration In B-type Model

In partly truncated terrains where the lateritic ferruginous layers have been preserved, a stone line may develop. In such profiles, the pisolitic horizon signature relates closely to that of the bedrock, the same as the base metals. In this context, Cu, and Mo may be found in the stone line. Zn is less resistant to this freely drained environment, and is therefore partially leached from the profile (Zeegers and Lecomte, 1992). Lead forms secondary minerals such as phosphates and carbonates; the last group of minerals is common in dry savannas (Gossens, 1974). In the lower horizons, elements such as Ni, Co and Zn can be retained by smectites and kaolinite.

If the residual soil is well developed, and not covered by transported overburden, lead and copper dispersion patterns will be developed but restricted to a very small area; the sampling grid should take this fact into account. In the pisolitic zone, both in background and anomalous areas, the content will be higher (Fig. 7.7a,b).

The truncation can remove all the pisolitic zone, in this case the saprolite becomes the most important sampling medium. Mineralogically, the saprolite is indicated by the predominance of smectites as the clay mineral. In the smectites Co, Ni can be concentrated, at the expense of a decline in the size of the dispersion haloes.

7.6. LATERITIC PROFILES IN HUMID TROPICAL TERRAINS (RAINFORESTS)

Humid tropical terrains (equatorial tropics) are typified by high annual rainfall and high mean temperature. Under these conditions most of the transformations due to weathering are related to in-situ hydrolysis, and leaching generally proceeds vertically.

The primary mineral assemblages are partly or totally transformed into a mixture of kaolinite, quartz and Fe-Al oxides (Millot et al., 1977 in Lecomte and Zeegers, 1992). Aluminium, Fe and Ti are the only major elements to be maintained or even enriched in the weathering profile whereas others are strongly leached. Among the base metals, those which follow the behaviour of Fe may be retained. This process leads to the formation of kaolinitic mantles which are part of the developing lateritic profiles (Lecomte and Zeegers, 1992). In most cases, the lateritic profiles in this environment do not have the peculiar ferruginous duricrust common in savannas. Apart from the lack of the cuirasse and the high thickness of the saprolite because of the intense weathering, element mobilities and dispersion are very similar to those observed in savanna climates (point 7.5).

7.6.1. A-type Dispersion Model: Pre-existing Profile Mostly Preserved

The common preserved lateritic profile in the rainforest environments has ben described by Nahon et al. (1980) as consisting of:

(1) ferruginous pebble layer, sometimes transformed into nodules embedded in a clay matrix in its upper part;

(2) soft iron crust;

(3) mottled argillaceous layer;

(4) saprolite.

7.6.2. Dispersion Model And Implications For Exploration In A-type Model

The degree of dispersion is sequential, increasing vertically upwards according to the zonation of the profile. In the saprolite the width of the anomalies may appear much greater than in the bedrock, having been enlarged by the hydromorphic dispersion. Nevertheless, the geochemical expression remains dominantly residual.

In the intermediate mottled and ferruginous horizon, the dispersion halo widens further, and the hydromorphic processes dominate over mechanical. Finally, in the degraded cuirasse, the dispersion is mostly controlled by the chemistry and mineralogy of iron; thus, the affinity of base metals with iron will be important for retention. As a consequence, the following is the distribution of base metals in rainforest lateritic profile:

(1) Cu, Zn, Ni and Co might be leached in the strongly weathering horizon (El-Ansary, 1986). These are the base metals normally abundant in soils from intermediate to basic rocks but strongly leached under deep weathering conditions. This can result in subdued anomalies if such metals are sought in this horizon; in such an environment, defined by high Al and Fe contents, attention should be paid to even weakly contrasted anomalies. It is relevant to notice that ferralitic weathering can be incomplete; thus, the metal- bearing minerals, such as the ferromagnesian minerals for Cu, Ni, Zn will remain and the content of these base metals will be slightly away from the normal behaviour (Zeegers, 1979).

(2) Mo, Pb and Cr will be retained or even concentrated in the iron rich horizon.

(3) In the saprolite, Ni and Co can occur as hosted by kaolinite or forming proper secondary minerals. The content of these base metals in saprolite reflects the signature of the bedrock.

Prospecting for Zn and Pb in Cameroon, Lecomte and Zeegers (1992) found that the dispersion haloes for these metals progressively enlarge in the upper part of the profile, reaching a maximum in the nodular horizon; here, the contrast was very weak due to strong leaching. Under these conditions of strong leaching, Zn can subdue the mineralization whereas Pb under high rainfall conditions forms stable secondary minerals such as phosphates and phospho-sulphates. These minerals can be identified either in soil sampling or in stream sediments. It can be inferred that the mobility of Pb after secondary stable minerals are formed, is basically mechanical. In the case of Zn which does not form stable secondary minerals under these conditions, its dispersion is essentially chemical, resulting in wide and

weak anomalies. Table 7.2 below gives the content of Pb and Zn in soil over a zinc mineralization.

Table 7.2: Comparison of selected base metals values in ore and soil sample (from Lecomte and Zeegers, 1992).

Element	Ore sample (ppm)	Soil sample (ppm)
Pb	4000	1100
Zn	10 000	90
Ag	10	2

Since the mobility of the elements is different, data obtained from soil surveys can suggest dual interpretation on the economic potential of the prospect. In highly leached environments where even stable trace metals may be leached, attention should be focussed on even small anomalies.

7.6.3. Dispersion Model And Implication For Exploration In B-type Model

This model applies to areas where the former lateritic surface has been dissected in such a way that the present topography intersects the pre-existing profile in the saprolite; thus, the main mineral is kaolinite. The geochemistry of such profiles will be dominated by those base metals which can be hosted in this mineral. The dispersion pattern is dominantly residual or hydromorphic where the saprolite is being transformed into soil. The target sampling medium in this case is the saprolite.

Base metals such as Co and Ni can be identified in the saprolite hosted by kaolinite or forming secondary minerals. Cu has been recognised as being enriched in the saprolite, if deeply leached from the upper horizons. Cu tends to be enriched in saprolite along with Co and Mn (El Ansary, 1986). This enrichment may either coincide or not with that of Ni.

In such cases, where the weathering profile is deeply truncated, the geochemical anomaly is mostly residual. The corresponding dispersion pattern is narrow. Thus, a close sampling grid may ensure the adequate identification and delimitation of the possible mineralized units.

8. BAUXITES

8.1. DEFINITION

Bauxites are clay-like sediments composed mainly of high-purity aluminium oxide (alumina) and iron oxide and practically devoid of silica. They were firstly described by Berthier in 1821 from Les Baux, in southeast France. Liebrich was the first to extend the term to cover lateritic weathering products rich in gibbsite (Liebrich, 1892 in Valeton, 1972). The term bauxite, therefore is used for lithified or unlithified, residual weathering products rich in alumina but low in alkalis, iron and silica. Bauxite may be unique in the diversity of its source, appearance, composition and geological disposition. It may be derived from almost any known rock type, provided that the required permeability and hydrological conditions are met (Grubb, 1973). The hydrological conditions suggest that most bauxites originated primarily through intense meteoric leaching in tropical and sub-tropical regions. Tectonic stability is critical because it allows chemical weathering to dominate erosional processes; continued stability is essential to encourage preservation of the weathered profiles (Gow and Lozej, 1993).

Bauxites consist primarily of a mixture of aluminium hydroxides: Gibbsite, boehmite and to lesser extent, diaspore. Other components, deleterious to aluminium, are clay minerals (mainly kaolinite), iron oxides, quartz, titanium oxides, water and a variety of other minerals. Figure 8.1 shows two bauxite profiles with the diagnostic mineralogical composition (Grubb, 1973). The coexistence of bauxite and kaolinite under seemingly identical tropical weathering conditions has long posed one of the major problems in ore genesis. Not only can extensive kaolinite and bauxite deposits be found within a single tropical region, they may also appear within the same profile (grubb, 1971).

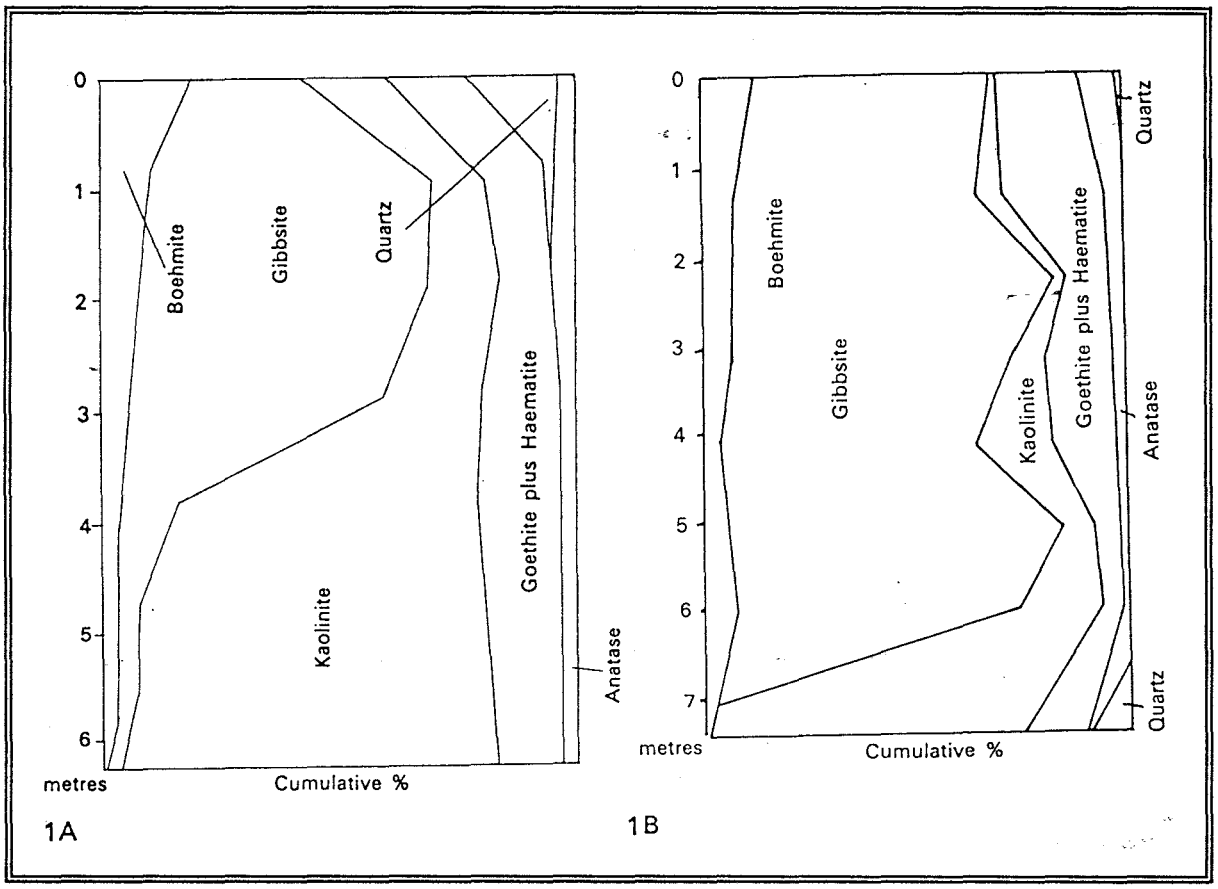


Fig. 8.1: Residual (A) and detrital (B) lateritic profiles showing diagnostic mineral variations (Grubb, 1973).

8.2. STRUCTURE AND WORLD DISTRIBUTION

Bauxites can be structureless, granular or earthly, pisolitic and concretionary, massive or stratified, or largely pseudomorphic after the parent rocks. Older bauxites that may have been subjected to burial are hard and compact, with boehmite and diaspore commonly being the aluminous minerals. More recent bauxites are generally softer, with gibbsite commonly being the dominant aluminous mineral (Gow and Lozej, 1993).

A well structured bauxitic profile (Fig. 8.2) may comprise the following horizons (Grubb, 1963):

(I) Yellow kaolinitic clay horizons, with numerous almost perfect authigenic quartz bipyramids.

(II) Red kaolinitic clay containing variable amounts of fine disseminated gibbsite and quartz

crystals.

(III) Bauxite horizon. This comes gradationally from the above horizon and is due to late-stage kaolinization of the fine disseminated gibbsite in the associated red clay and also of larger bauxite concretions and pisolites at the base.

(IV) Mottled red zone which passes to the parent rock.

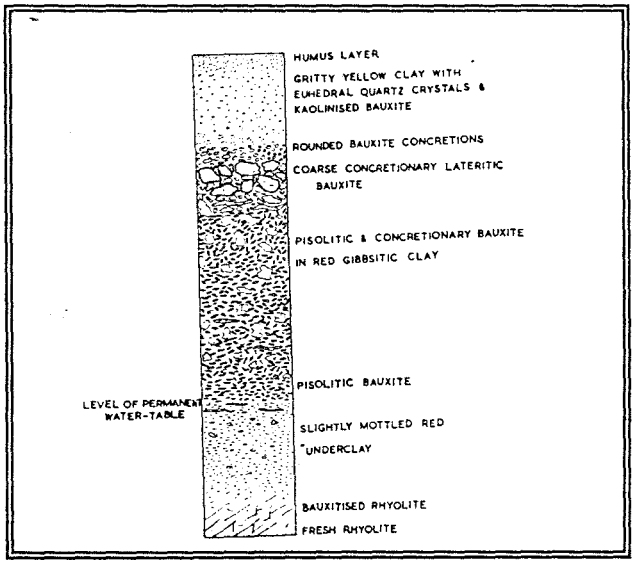


Fig. 8.2: Typical bauxitic profile (from Grubb, 1963).

The distribution of bauxites in geological time seems to indicate that Late Proterozoic, Middle to Late Cretaceous and Middle to Late Tertiary were favourable periods for bauxite formation (Gow and Lozej, 1993). This distribution is essentially a result of climatic conditions which favoured sustained weathering processes leading to the leaching of several chemical elements and enrichment of aluminium hydroxides.

The geographical distribution of bauxites (Fig. 8.3) suggests that the actual tropical environment is one of the most important in the development of these soils and coincides with the area covered by the lateritic profiles (Fig. 5.3).

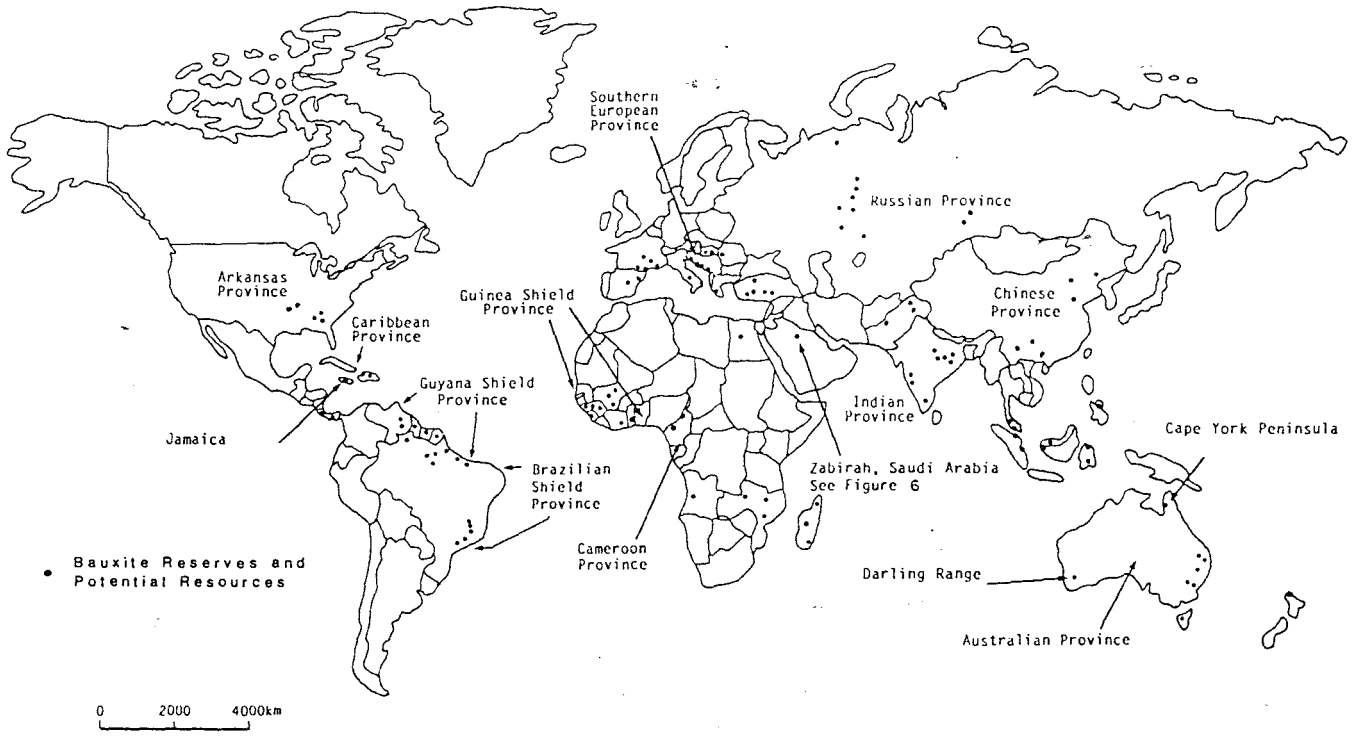


Fig. 8.3: World bauxite distribution (from Gow and Lozej, 1993)

8.3. BASE METALS IN BAUXITIC PROFILES

The process of successive Si and Fe removal from the profile leads to a continuous Al-enrichment in lateritic bauxites and in pure bauxites. During this process, base metals are mobilized and leached from the environment. In some cases they may be concentrated at specific horizons.

Certain base metals may become enriched to such an extent as to render deposits mineable or are mined as by-products. This is the case for Ti, Ni, Co and Cu (Valeton, 1972). The geochemical behaviour of base metals in igneous, metamorphic or sedimentary tropical weathering and subsequent formation of bauxites is very similar. The most important in this process is the availability of these base metals. According to Sinclair (1967), the content in base metals in bauxite precursor material is normally high (Table 8.1). The highly leaching weathering conditions in this environment are responsible for the removal of base metals normally observed in bauxitic profiles. These elements are partially redistributed along the profile.

Table 8.1: Base metals in bauxites and bauxitic soils derived from limestone, values in ppm (Sinclair, 1967).

	Cr	Ni	Cu	Pb	Zn
Bauxites and bauxitic soils	780	420	170	100	210
Limestone residues	870	1720	310	120	120
Cretaceous rocks	20	10	65	<30	60
Soil on Cretac. rocks (-80 mesh fraction)	35	15	70	30	75

The partitioning of the base metals in a bauxitic soil profile is dependent upon the mineralogy of the bauxite. Co and Ni are normally hosted in ferromagnesian minerals. These minerals are normally converted to goethite and limonite during the formation of bauxite; thus, goethite and limonite are the only minerals likely to contain Co and Ni. Nickel can also occur in ferric hydroxide minerals in kaolinitic clay and bauxite.

The similarities in the behaviour of these elements during the bauxite formation from weathering of diabase were established by the correlation coefficients employing log-transformed concentrations data (Scorin and Puchelt, 1987). The concentration ratios were calculated using the Mackenzie and Murata equation (Mackenzie and Murata, 1952 in Scorin and Puchelt, 1987):

$$C_{bauxite} / C_{Initial\ Rock} \qquad (8.1)$$

where C is the concentration of the base metal in each rock type.

For this purpose, the average concentration of any element in the entire profile (or the ferruginous bauxite or the bauxite ore horizon) was divided by the concentration of the same base metal in the diabase. The results are the enrichment factors for each base metal and are presented in Table 8.2.

Table 8.2: Enrichment factor for the bauxitic iron ore relative to the precursor diabase (extracted from Scorin and Puchelt, 1987).

Base metal	Laterite	Ferruginous bauxite	Bauxite
Ni	2.21	2.21	2.29
Co	0.15	0.16	0.11
Cu	0.47	0.52	0.29
Zn	0.30	0.30	0.31
Cr	1.17	1.69	2.21

The elements that were enriched are Ni and Cr. Copper and Zinc were less leached and Co was deeply depleted if compared with the contents of the diabase Table 8.2. The partitioning of these base metals can be seen from the correlation coefficients. Ni and Zn are more enriched in bauxites with 0.9 and 0.88 as the correlation coefficients respectively. Nickel shows a good correlation coefficient with ferruginous bauxite (0.80); thus, it will also be found in iron rich horizons. Cobalt and Copper were mainly concentrated in the alumina rich ferruginous bauxites.

This base metals distribution in bauxitic profiles is similar to that described in Western Australia (Davy and El Ansary, 1986); where Cu and Ni tend to be very low in the hardcap but are locally concentrated at the bottom of the hardcap or in the upper clay zone. Copper, in particular, then tends to be enriched in the base of the saprolite along with Co. The position of its maximum enrichment in the upper part of the profile either coincides with, or is slightly below the equivalent enrichment for Ni. Cobalt is strongly leached throughout the profile and reconcentrated at the contact saprolite-bedrock (Table 8.3). Molybdenum is mobilized and reprecipitated in the iron rich hardcap.

Table 8.3: Behaviour of base metals in four residual lateritic bauxite profiles in Western Australia (extracted from Davy and El-Ansary, 1986).

Description	Profile 1	Profile 2	profile 3	Profile 4
Leached within clay zone, no surface enrichment.	Cu, Ni	----	Cu, Ni, Zn	Ni, Cu, Zn
Component leached at the top of the profile concentrated near bedrock-saprolite boundary.	Co	Cu	Co	Co
Mobilized and reprecipitated, with values in hardcap or upper clay zone similar to those in bedrock.	Cu, Ni	Ni	Cr, Mo	Cu
Mobilized and reprecipitated, enriched in iron hardcap, relative to bedrock.	Cr, Mo	Mo	----	Mo

Wulfenden (1965) compared the content of andesite and the subsequent bauxite in Mungu Belian, Malaysia and concluded that Ni and Co were depleted in bauxites. The depletion of these base metals is enhanced by the reduction of Fe^{3+} in the goethite to Fe^{2+} which passes into the solution, thereby lowering the goethite content and releasing the adsorbed Co and Ni. If Fe and Al are retained in a profile, then, Co and Ni are residually enriched. Nickel will be carried in Goethite and Co, besides in goethite, may appear in the Mn minerals. Thus, in a soil profile where essentially Fe and Al are conserved, Mn, Co and Ni demonstrate parallel behaviour suggesting that the same controlling mechanism is operative (Norton, 1973). The disintegration of goethite at negative Eh values seems to be one of the preponderant factors leading to the release of Ni and Co. When pure bauxite forms, Fe is removed from the profile. Selective removal of Fe from the soil with retention of Al requires unique pH and Eh conditions. Very low pH (below about 3.5) will mobilize Al, and at high Eh, Fe is residually enriched, whereas at low pH and Eh, Fe is mobilized (Norton, 1973).

The behaviour of Co and Ni is very similar to that of iron during the bauxitization. Furthermore, those factors which cause residual enrichment of Al with removal of Fe in soils

will cause significant depletion of Co and Ni in the profile. These metals are then concentrated at the base of the profile because of the precipitation from downward percolating solutions. Many karst bauxites deposits in southern Europe are enriched with Mn, Ni and Co in the basal horizon. Such a horizon is mined as nickel ore in the bauxites of the Lokris region in Greece (Valeton, 1972).

Copper and Molybdenum are more strongly enriched than Al in bauxitic profiles (Gordon et al.,1958 in Valeton 1972). Concentration ratios are 8 and 3.2 for Cu and Mo respectively (Gordon and Murate, 1952). Molybdenum is known from its close relation with goethite and hematite; thus, the high concentration of Mo is related to the iron concentration (Table 8.3). Copper concentrates at the base of the iron-rich horizon but also appears enriched in the saprolite together with Co. Sinclair (1967) Table 8.1, also reported moderate concentration of Cu in limestone bauxites of Jamaica.

Lead, although concentrated does not show a very remarkable trend in a bauxitic profile. The concentration ratio of Pb in Arkansas bauxites was 1 (Gordon and Murate 1952), suggesting that this base metal is less sensible to the bauxitization process.

In British Guiana bauxites (Harden and Bateson, 1963), the strong accumulation of iron occurs above the bauxite ore body (Fig. 8.4), overlying the kalinitic clay. This zonation leads to the recognition of the iron-rich horizon as equivalent to a pedogenic B horizon with the bauxite representing a leached A horizon. The zone of iron accumulation is characterized by the presence of abundant ferruginous nodules which indicate a zone of iron concentration such as is frequently found at the upper level of the water-table (Harden and Bateson, 1963). The underlying kaolinitic clay would thus represent the parent material (saprolite) or C horizon. The aforementioned zonation of the profile is important in understanding the distribution of base- metals. From the ore zone the metals are leached downward and accumulated in the iron rich zone. Base metals such as Ni, Co, Mo and to a certain extent Cu show good correlation with goethite; thus, they may be found in the base of the bauxitic profile.

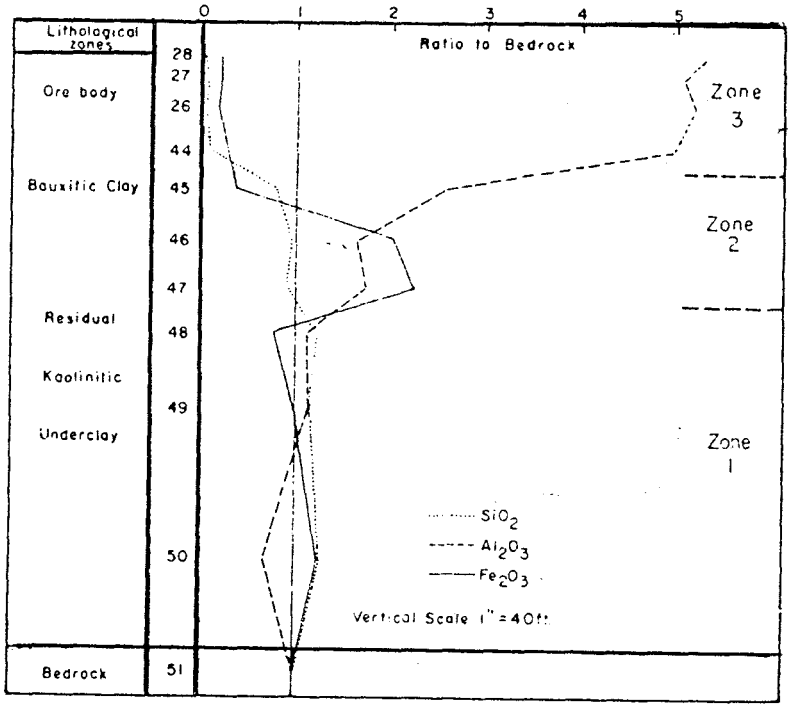


Fig. 8.4: Zonation and composition of a bauxitic profile in terms of major elements (from Harden and Bateson, 1963).

8.4. BASE METALS EXPLORATION MODEL

Bauxites are developed in tropical and subtropical areas where relative tectonic stability has prevailed.

The highly leaching conditions during the bauxite formation promote the removal of the most of the base metals which, as soluble cations, percolate downwards and in some cases are concentrated in the base of the profiles. The surface expression of most of the base metals does not appear to reflect bedrock concentration closely, because of this intense leaching.

Nickel and cobalt are commonly depleted throughout the profile, but economic residual accumulaton of these two base metals has been reported as common in the base of the bauxitic profile. This is particularly common in karst bauxite and karstificated jurassic limestone where the grades may reach 2.67% and 0.05% for NiO and CoO respectivelly (Valeton, 1972). Geochemical exploration for these commodities in this environment is usually orientated to the

base of the profile, when the aim is to identify the residual accumulation of Ni and Co. When the objective is the characterization of the bedrock, on iron-rich horizon will yield the best contrast because of the relationship between Ni or Co with iron (Table 8.2). Depending on the bauxitic profile development, some authors have recognised that the base of the bauxite is rather chemical accumulation zone than residual, due to the concentration in this horizon of goethite and hematite (Fig. 8.4). In this case, sampling this horizon will provide reliable information for bedrock description.

Molybdenum, lead and copper are not known as developing economic residual accumulation during bauxite formation. Nevertheless, they can be used to characterize the bedrock. Molybdenum and copper are strongly enriched in bauxite profile and they are concentrated in iron rich horizons. Samples should, therefore, be collected where goethite and hematite are concentrated. Surface copper , even though depleted, has been used to identify potential areas of mineralization (Davy and El-Ansary, 1986). In the Scorin and Puchelt (1987) profiles, base metals studies should be orientated to the ferruginous horizons whereas in the Harden and Bateson (1963), (Fig. 8.3) the base of the bauxite ore zone may yield the best contrast for copper and molybdenum.

Lead shows a concentration ratio of 1 (Gordon and Murate, 1952) suggesting that this commodity is neither accumulated nor removed during the bauxitization process. Lead may be used to infer the content of base metals in precursor rock.

9. SUMMARY AND CONCLUSIONS

Tropical terrains are typified by a thick soil cover that is due to intensive and pervasive weathering. Base metal mineralization, in such environments, undergoes deep alteration, obliterating the primary dispersion features. From the primary mineralization, base metals are released and redistributed according to their physical-chemical behaviour in the secondary environment.

The geochemical dispersion and exploration models summarized herein attempt to synthesize the nature and characteristics of the surface expression of the base metal mineralizations when the primary rock is deeply weathered. They take into account the process of metal release, mobility and the factors controlling their concentration in specific horizons in a soil profile. Ideally, it should be possible to use such models predictively when planning surveys, to anticipate the mechanisms of dispersion, select the appropriate sample media and estimate the nature and significance of anomalies (Butt and Zeegers, 1992).

Although most of the world's accessible ore deposits have already been found, in many areas, however, a thick soil cover obscures other ore-deposits from view. In such cases, where classical geological investigation fails as a result of poor outcrops, geochemical field methods may still establish anomalous distribution patterns of base metals in stream sediments and mostly in soils covering such hidden deposits, or even in gossanous remnants of leached sulphides. It is common in such areas, in exploration for mineral deposits, to sample and evaluate as follows:

1. Streams and stream sediments; in order to establish abnormal contents of base metals, indicating the possible existence of ore deposits upstream. In this case, samples can be water, heavy minerals, stream sediments and Mn and/or Fe coatings.
2. Soil samples; the soil development process can lead to the formation of a lateritic profile or a bauxitic profile; in each case there are specific factors controlling the redistribution of base metals; therefore, sampling is often done considering such factors.
3. Gossan sampling and evaluation; most of the base metal mineralizations in tropical terrains developed a ferruginous cap resulting from the highly leaching conditions. A geochemical evaluation of such gossans requires an in situ and laboratory study of the fabrics, mineralogy

and geochemical signature of the precursor sulphide mineralization to assess its potential to be an economic source.

Outlined below are some further pointers to exploration for base metals in tropical terrains:

In gossan recognition and evaluation: Discovery and recognition of true base metal gossan is hambered not only by the lack of outcrops but also by the wide variety of other types of ironstone (Moeskops, 1977). Prior to sampling, an ironstone outcrop should be mapped in detail, with special note being taken to outcrop extension, the host rocks, the structures and continuity of the ironstone.

The fabric, mineralogy and geochemistry of gossans are largely determined by the pH of the oxidizing environment and this is a function of the initial mineralogy. Boxwork fabrics are best preserved when the environment has a high pH. Under these conditions no Fe^{2+} can remain in solution, being immediately precipitated on crystal faces, cleavages, twin planes and grain boundaries. In gossan evaluation, the secondary minerals formed from the weathering of the country rocks are of paramount importance because they may incorporate some target and pathfinder base metals, therefore, a careful search for secondary minerals and their composition may indicate the nature and composition of the precursor sulphide assemblage. This can be illustrated by the alunite-garosite family which incorporate either Pb or Cu when such base metals are available in the environment.

Precious and volatile elements have been used at the confirmatory stage of Ni gossan evaluation (McGoldrich and Keays, 1981). The absolute content of Ir can provide a fairly reliable guide to the Ni grade of the parent sulphides and the oxide zone from some sulphide gossans retains Ir and Pd at levels which reflect the composition of the fresh disseminated mineralization. Data presented by Moeskops (1977) suggests that Pt, Pd and Se are very important in the confirmatory stage of Ni gossan evaluation.

In lateritic profiles: The mineralogy of the constituent horizons has a determinant role in the retention or leaching of base metals in the profile. In the upper ferruginous horizon, where goethite and hematite are predominant, large amounts of Mo which is adsorbed in those iron minerals, will be identified. The geochemical signature of other base-metals in this

horizon is very subdued due to intense leaching but it is still preserved. The recognition of such weak but significant geochemical responses in the surface horizons in deeply weathered terrains requires the use of suitable sampling and analytical techniques. In the lower horizons, in the saprolite, elements such as Cu, Zn, Ni and Co can be retained by secondary silicates such as kaolinite and smectites. Nevertheless, the use of the saprolite as a sampling media is restricted due to the required close sampling intervals as the secondary dispersion is reduced.

The quality of the geochemical response that is obtained in lateritic soil profiles strictly depends on the horizon which is sampled. The poorest response for the bulk of base metals is obtained in the surficial horizons. These are commonly strongly leached. Conversely, if the saprolite is sampled, a strongly contrasting response for Cu, Zn, Ni and Co will be identified. This normally provides details about the lithology, the mineralization itself or any features associated with primary halo or hydrothermal alteration (Zeegers and Lecomte, 1992).

In bauxitic profiles: Where Al-rich rocks undergo deep weathering, bauxites and bauxitic laterites may develop. In these profiles Ni and Co are depleted throughout the profile, being concentrated at the base of the profile, in the bedrock-saprolite contact (Davy and El Ansary, 1986). Some karst bauxite deposits in southern Europe are enriched with residual Ni and Co in the basal horizon. Such horizons are is mined as Ni ore in the bauxite of the Lokris region in Greece (Valeton, 1972). Molybdenum is mobilized and reprecipitated in iron-rich horizons; lead, although concentrated does not show any preference to specific horizons in these profiles.

In summary, in this environment where the thick soil cover severely hampers direct prospecting and geological mapping, geochemical exploration, based on the behaviour of each base metal, can still identify the surface expression of the mineralization, becoming one of the most effective and reliable techniques of mineral exploration for base metals in tropical terrains.

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