GEOCHEMICAL EXPLORATION IN ARID AND SEMI-ARID ENVIRONMENTS TR 83-14

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ABSTRACT

Anomalous element distributions within the regolith result from chemical adjustments of the earth's surface to prevailing climatic conditions. Because of the lack of moisture in the arid environment, chemical equilibrium related to paleoclimates is largely maintained. Mechanical or clastic dispersion dominates arid weathering and hence the exploration approach is largely dictated by the degree of preservation of the paleoregolith. Arid environment geochemists thus have to contend with surface materials ranging from laterite and calcrete in areas where the imprint of aridity is minimal, to more conventional sample media such as bedrock, stream sediment and lithic soils in actively dissecting areas. Extraction techniques are designed specifically to isolate clastic dispersion trains. Thick mantles of aeolian and water-borne overburden characterise desert lowlands and are a challenge to the exploration geochemist. Techniques showing the most promise in these areas include groundwater geochemistry, vapour geochemistry, surface microlayer geochemistry, geobotany and biogeochemistry which attempt to isolate gaseous and weak hydromorphic, ore-related trace-element dispersions. Termite mound sampling yields convincing results and appears to be an under-utilised geochemical approach.

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INTRODUCTION

The arid and semi-arid areas (Fig. 1) occupy a third of the earth's land surface (Cooke and Warren, 1973), yet standard texts on geochemistry concentrate mainly on geochemical techniques applicable to humid environments, barely mentioning the exploration implications of land-forming processes of the arid environment to surface geochemical adjustments. An understanding of these environmental factors is essential in the formulation of exploration programs and in the intelligent interpretation of results. Levinson (1980, p.626) comments : the "study of exploration techniques to be used in arid environments, particularly deserts, has been sorely neglected", and recommends this as a topic demanding immediate research.

The objective of exploration geochemistry is to detect anomalous patterns in the element distributions within the surficial environment that may be related to mineralisation. Common sampling media are rocks, soils and other types of overburden, ground and surface waters, gases and particulates, and biological materials. The chemical make-up of these sample media results from the continuous chemical adjustment of their mineralogy to changing processes in a dynamic environment.

The effective use of geochemical techniques depends on an understanding of the constraints imposed on geochemical interpretation by the interacting roles of tectonics and climate on the earth's surface and resulting geomorphology as well as geochemical overprints related to past climatic epochs. The format adopted here thus stresses the relationship between the main stages of landscape evolution under the arid climatic regime, and the behaviour of element mobility within the secondary environment. The discussion is illustrated by published case studies. Original orientation drainage surveys across the Haib porphyry-type copper mineralisation in southern Namibia and a volcano-sedimentary Zn-Pb occurrence in Namaqualand, characteristic of two very different landscape settings, are presented.



Figure 1. Arid regions of the world. Polar arid regions not shown. (From : Cooke and Warren, 1973).

Exploration techniques employed in the search for hydrocarbons and uranium are not included as these have received ample coverage in the journals. Excluded also are high-latitude polar deserts.

ARID AND SEMI-ARID ENVIRONMENTS

Climatic classifications are legion. Schemes used here are based on those parameters which most strongly affect the redistribution of elements within the supergene zone and into the regolith. Mechanical, and to a greater extent, chemical weathering is controlled primarily by precipitation and temperature, the latter determining the precipitation to evaporation ratio.

The Köppen system combines average annual temperature and precipitation characteristics with soil and vegetation distributions. Five major climate groups are designated by the capital letters A to E (Fig. 2a). Subgroups within the major groups are given a second letter (Fig. 2b), and a third letter may be added to quantify precipitation and temperature variations (Fig. 2c). The letters S and W are applied only to the dry B climates yielding the two combinations, BS (semiarid steppes) and BW (dry arid deserts). Köppen climatic groups A, C, D, and E are defined by temperature averages, whereas group B is defined by precipitation/evaporation averages.

Meigs' (1953) scheme is based upon Thornthwaite's moisture index, which relates the adequacy of precipitation to the annual hypothetical evaporation and transpiration of natural vegetation. In this classification the outer limit of dry lands is taken at the -20 value of the moisture index. Areas with a moisture index of between -20 and -40 are defined as semi-arid, and those areas less than -40 as arid. Within the arid boundary Meigs recognised extremely arid areas, which are defined as those where at least 12 consecutive months without rainfall have been recorded and where there is no seasonal rhythm of rainfall. The semi-arid, arid and extremely arid zones are further classified according to the time of year when precipitation occurs and the mean temperature of the warmest and coldest months. The pattern produced by this scheme is shown on Fig. 1. Meigs' arid and extremely arid lands coincide with Köppen's deserts (BW subgroup), while the areal distribution of his semi-arid

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regions corresponds to Köppen steppe climates (BS subgroup).

- A Tropical climates. Average temperature of every month is above 64.4°F (18°C). These climates have no winter season. Annual rainfall is large and exceeds annual evaporation.
- B Dry climates. Potential evaporation exceeds precipitation on the average throughout the year. No water surplus; hence no permanent streams originate in B climate zones.
- C Warm temperate (mesothermal)¹ climates. Coldest month has an average temperature under 64.4° F (18°C), but above 26.6°F (-3°C); at least one month has an average temperature above 50°F (10°C). The C climates thus have both a summer and a winter season.

D Snow (microthermal)² climates. Coldest month average temperature under 26.6°F (-3°C). Average temperature of warmest month above 50°F (10°C). that isotherm coinciding approximately with poleward limit of forest growth.

E Ice climates. Average temperature of warmest month below 50°F (10°C). These climates have no true summer.

(a) The five major climatic regions

- S Steppe climate: A semi-arid climate with about 15 to 30 in (38 to 76 cm) of rainfall annually at low latitudes. Exact rainfall boundary determined by formula taking temperature into account.
- W Desert climate: Arid climate. Most regions included have less than 10 in (25 cm) of rainfall annually. Exact boundary with steppe climate determined by formula.
- f Moist. Adequate precipitation in all months. No dry season. This modifier is applied to A. C. and D groups.
- w Dry season in winter of the respective hemisphere (low-sun season).
- Dry season in summer of the respective hemisphere (high-sun season).
- m Rainforest climate despite short, dry season in monsoon type of precipitation cycle. Applies only to A climates.

(b) Codes for subgroups

a With hot summer: warmest month over 71.6°F (22°C) (C and D climates).
b With warm summer; warmest month below 71.6°F (22°C) (C and D climates).
c With cool, short summer: less than four months over 50°F (10°C) (C and D climates).
d With very cold winter; coldest month below - 36.4°F (-38°C) (D climates only).
h Dry-hot: mean annual temperature over 64.4°F (18°C) (B climates only).
k Dry-cold; mean annual temperature under 64.4°F

(18°C) (B climates only).

(c) Annual temperature precipitation quantifiers

Figure 2. The Köppen classification system of world climates. (From : Strahler, 1975).

Geomorphological processes in semi-arid lands are very similar to those in the more arid areas (Cooke and Warren, 1973; Mabbutt, 1977). Hence an understanding of the general concepts of landforming processes operative in the extremely arid, arid and semi-arid regions, as well as soil-landscape relations, is essential for the successful application of geochemical methods in these areas.

The factors that directly affect the operation and balance of geomorphic processes, within broad limits set by

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climate, are geologic structure and relief (Mabbutt, 1977). In this scheme the world deserts can be grouped into two broad types, namely the deserts of the shield and platforms, and the mountain-and-basin deserts of tectonically more active zones.

Shield and platform deserts comprise the arid regions of Africa, Arabia, Australia and India. Typical landforms include broad plains on granitic rocks of the exposed shields (Western Australia), and tablelands and basin lowlands over flat-dipping sediments (Sahara). High relief is associated with ancient orogenic belts and areas of younger igneous activity (central Sahara, Sinai). These are limited in extent and rarely is relief sufficient to moderate aridity or to introduce forms due to frost action.

Similarity of relief stems from a common long and stable tectonic and geomorphic history, under which ancient landforms have survived extensively. Extensive deep weathering and planation of the shields under savanna regimes in the earlier Cenozoic, as indicated by remnants of laterite, was followed by stripping of weathered layers from higher parts and deposition in the low-lying areas, with concomitant development of endorheic drainage, playas, and thin sheets of calcrete or silcrete, with progressive increase in aridity. On this trend were superimposed the effects of Quaternary wetter and drier phases, the former associated with increased fluvial activity in the piedmonts and the latter with the extension of sand dunes in the remote lowlands.

The effects of Eocene-Oligocene deep lateritic weathering are particularly evident in the stable structural tablelands of the platforms in Western Australia which are reinforced with an indurated layer of laterite overlying deeply leached transported or residual overburden. Exploration in these areas relies heavily on the recognition of indicator elements, which due to their immobility under humid oxidising and subsequent arid conditions, are substantially more abundant in the weathered orebody than in the surrounding rock. Mountain-and-basin deserts are characterised by the juxta-position of mountain and plain, commonly with sufficient local relief to generate climatic contrasts. Seasonal floods from the uplands, locally fed by snowfields or glaciers, carry abundant debris from steep slopes in fractured rock, its breakdown often accelerated by frost. At the sharp junction of mountain and plain, often tectonically determined, coarse alluVium is deposited on gravel fans. Further down slope are plains of finer alluvium, partly saline, and playas. Basin sediments may attain a great thickness. Due to the rapid alternation in relief, the water table is frequently at the surface in the valleys where playas form evaporative terminals where salts concentrate.

Mountain-and-basin deserts include the cold middle-latitude desert and steppe climates (portions of the Basin and Range Province in western USA), and parts of the low latitude west-coast desert climates of the South American Andes.

The Secondary Environment in Arid Terrains

Desert weathering is characterised by superficiality (Mabbutt, 1977), as shown by shallowness of soil profiles and weathering mantles and the abundant accumulation of surface salts and patinas (desert varnish). Mechanical weathering processes predominate over chemical processes in arid and semiarid lands because the former processes are enhanced by the high percentage of exposure and the latter reduced by low humidities and resulting limited plant cover.

Mechanical Weathering

Insolation weathering refers to mechanical failure of rock surfaces caused by the differential expansion of the various minerals in response to steep, diurnal temperature gradients in the near surface layers of rocks. This is not thought to contribute significantly to direct breakdown of rock but the repeated stressing of a rock below that of its relaxation period tends to increase jointing which in turn assists clastic disintegration. Frost weathering results from pressures exerted by the volumetric expansion of water when it freezes in confined spaces, and only actively contributes to the breakdown of rocks in high altitudes such as the mountainous Mojave Desert, California (Cooke and Warren, 1973). The abrading effect of wind-blown sand and the grinding and scouring of rocks in torrential desert stream flows causes localised but extensive rock destruction.

Physico-chemical Weathering

In desert environments strong surface heating and generally low humidity limit moisture penetration in the rock, resulting in rapid upward capillary return through excessive evaporation. Weathering reactions are thus restricted to a relatively thin surficial layer.

Hydration reactions become increasingly important where rock material is reduced to colloid dimensions, by incipient weathering in minute cracks and fissures. Arid weathering, with restricted moisture and non-acid environment, favours the development of montmorillonite (Krauskopf, 1979). On hydration, or increase in moisture content through interlayer adsorption, this clay undergoes marked expansion thus aiding in the breakdown of the rock (Mabbutt, 1977).

Salt weathering leads to rock disintegration through stresses set up by volume change during hydration reactions or crystal growth (Mabbutt, 1977). The salt source may be oceanic, from groundwater in nearby playas, or products of chemical rock leaching. Salt weathering is most effective in porous rocks and is relatively important in coastal deserts where high salinity and atmospheric humidity are combined (Namaqualand, Israel, and the coastal Atacama desert).

Chemical Weathering

The arid environment imposes constraints which radically alter the relative effectiveness and range of the chemical changes accompanying chemical weathering in moister climates. The chief limitation is the lack of water in the weathering zone, its shallow penetration and rapid return to the surface by capillarity and hence its very restricted residence time at the weathering front. The lack of humic acids and CO₂ result in an oxidising, alkaline weathering environment in which chemical reactions seldom attain completion before erosion. Desert debris therefore is generally coarse-textured containing such unstable minerals as sulphides, biotite, feldspars, and amphiboles, and little or no clay (Ayalon, 1976). On stable landscapes (plateaux, tops of mesas) where erosion is minimal, a distinct clay horizon may develop in soils (Birkeland, 1974). The arid and semi-arid weathering cycle is thus characterised by mechanical dispersion with hydromorphic patterns developed in saline desert environments.

Soils of Arid Regions

Arid region soils are markedly different from soils in the more humid regions. They are characterised by a low level of organic matter, a calcium carbonate accumulation within 1.5m of the surface and hence a slightly acid to strongly alkaline reaction, weak to moderate profile development, coarse to medium texture, and low biological activity. Desert pavements are frequently developed on these soils. Soluble salts (halite, gypsum) may be present in quantities sufficient to appreciably alter the mobilities of trace elements in the surficial environment.

The usual topographic sequence of arid-zone soils begins with shallow rocky soils on barren mountains and hills, progressing downslope to coarse-textured and deeper soils on the dissected upper alluvial fans. This is followed on the lower fans and pediment slopes by finer-textured and deeper soils with more well-defined carbonate and clay horizons (Fig. 3). Sand dunes may cover part or all of the fan and pediment slope soils. At the lowest levels two quite distinct soil types may occur. If the watershed drains into a closed basin (playa), fine-textured saline or gypsiferous soils are likely to be dominant. In areas of open drainage, soils of the stream floodplain usually are of variable texture and nonsaline. There are many exceptions to the above generalisations. Texture, structure, salinity and calcrete content may vary markedly due to physiographic position, bed rock type, vegetation density, age of the land surface and the type of desert climate.



Figure 3. Soil-landscape relations in arid regions. Rock outcrops have no significant soil cover, Torriorthents are weakly developed, Calciorthids are more developed, and Haplargids show the most development in this sequence. Torripsamments and Torrifluvents are underdeveloped sands and recent alluvial soils, respectively. (From : Dregne, 1976).

Mobility in the Arid Secondary Environment

Weathering in deserts produces large volumes of mechanically derived rock detritus and lesser amounts of soluble salts which together constitute the regolith. Probably in excess of 50 percent of geochemical techniques in mineral exploration concentrate on the recognition of clastic and hydromorphic dispersion patterns within this surficial aggregate. The general alkaline nature of arid soils, the formation of calcrete or gypcrete layers within the soil profile, strongly influences element mobility within soils (Levinson, 1974), the ion-exchange capacity of montmorillonite (Krauskopf, 1979), and the uptake of trace elements and their stability in the secondary environment is also sensitive to Eh (oxidation potential). Levinson (1974, p. 142) lists 10 further variables affecting mobility.

Even within the poorly developed desert soil profiles, pH may vary greatly over short distances, both vertically and laterally, depending on moisture content, CO₂-pressure in the soil air, and the distribution of alkaline salts. Most surfaces coated with organic colloids are acid, probably even in alkaline ground (Hunt, 1972). The term salinity generally refers to the chlorides of the alkalis or alkaline earths; alkalinity generally refers to their sulphates or carbonates. Depending on the salts present, soils may be saline without being alkaline (halite-rich ground), or alkaline without being saline (calcreted soil), or may be both.

In considering applications of mobility to practical geochemical problems it is necessary to determine the extent to which movement is chemical or mechanical. If processes are dominantly mechanical as appears to be the case in arid and semi-arid areas, only the various gravitative dispersion mechanisms need to be considered. If dispersion is mainly hydromorphic (chemical), sulphide oxidation, element mobility in the secondary environment and direction of groundwater movement are important criteria needing investigation. Both clastic and hydromorphic dispersion is reflected in the element content of plants. These biogenic patterns tend to reflect local bedrock variations in areas of shallow soil and groundwater chemistry in areas of thick overburden.

Hydromorphic Dispersion

Many attempts have been made to determine the relative mobility of trace elements in the secondary environment. Andrew-Jones (1968) shows that relative mobilities of elements in the supergene environment is pH and Eh dependent (Fig. 4). This table shows the pH dependence of the mobility of some elements, particularly the group Cu, Co, Ni, Mg, Ag, and Au which has medium mobility under oxidising conditions and high mobility under acid conditions, and becomes immobile under neutral to alkaline (arid) conditions. Similarly, Zn, which is highly mobile under oxidising and acid conditions is relatively immobile under arid conditions. Most of these elements are pathfinders for their host deposits but will have only limited dispersion halos in calcrete environments. Molybdenum, vanadium and selenium have very high mobility in neutral to

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alkaline media, and are used as pathfinders for porphry coppers, secondary uranium, and sulphide ores respectively.

Environmental conditions				
Relative mobilities	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, 1, 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, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl Li	Si, P, K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl, Fe, Mn	Si, P, K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl, Fe, Mn	Si, P, K, Fe, Mn
Very low to immobile	Fe, Mn, Al, Ti, Sn, Te, W, Nb, Ta, Pt, Cr, Zr, Th, Rare earths	Al, Ti, Sn, Te, W, Nb, Ta, Pt, Cr, Zr, Th, Rare earths	Al, Ti, Sn, Te, W, Nb, Ta, Pt, Cr, Zr, Th, Rare earths, Zn, Cu, Co, Ni, Hg, Ag, Au	Al, Ti, Sn, Te, W, Nb, Ta, Pt, Cr, Zr, Th, Rare earths S, B, Mo, V, U, Se, Re, Zn, Co, Cu, Ni, Hg, Ag, Au, As, Cd, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl

Figure 4. Relative mobilities of the elements in the supergene environment. (From : Brooks, 1972).

A more quantitative way of expressing the empirical relationships tabulated in Fig. 4 is to consider the pH at or above which metals in dilute solutions tend to precipitate as hydroxides; known as the pH of hydrolysis. In Fig. 5 several elements are presented in order of increasing pH of hydrolysis. Thus, in calcreted soils with a pH of 8.5 - 9, only Mg²⁺ is mobile while the remaining elements listed will be relatively immobile. Zn²⁺, with a pH of hydrolysis of 7 will therefore show larger dispersion halos than Cu²⁺ (pH of hydrolysis of 5.3) in the neutral to mildly alkaline surficial soils of semi-arid regions. In neutral stream sediments, elements with a pH of hydrolysis below 7 will precipitate close to their point of entry into the system, from whence onwards dispersion is essentially mechanical.

Acidified groundwater associated with near surface oxidising sulphides creates localised conditions under which

such elements as copper and lead, normally immobile in arid environments, are soluble. Metals will remain in solution until the neutralising effects of country rocks lower the pH below the precipitation barrier, thus significantly enlarging the dispersion halo. The surface and near surface geochemistry at the Otjihase Prospect, Namibia clearly illustrates the increased mobility of copper in an arid environment.

Element	pН	Element	pН	Element	pН	Element	pН
Fe+3	2.0	Al+3	4.1	Cd+2	6.7	Pr+3	7.1
Zr+4	2.0	U+6	4.2	Ni+2	6.7	Hg+2	7.3
Sn+2	2.0	Cr+3	5.3	Co+2	6.8	Ce+3	7.4
Ce+4	2.7	Cu+2	5.3	Y+3	6.8	La+3	8.4
Hg+1	3.0	Fe+2	5.5	Sm+3	6.8	Ag+1	7.5-8.0
In+3	3.4	Be+2	5.7	Zn+2	7.0	Mn+2	8.5-8.8
Th+4	3.5	Pb+2	6.0	Nd+3	7.0	Mg+2	10.5

Figure 5. pH of hydrolysis (hydroxide precipitation) of some elements from dilute solutions. (From : Levinson, 1974).

The Otjihase Besshi-type cupreous pyrite deposit is hosted in a banded magnetite quartzite unit within chloritic schists and is located ∿ 20km northeast of Windhoek (Fig. 6). The climate is warm to hot, semi-arid with an annual rainfall of 370 mm (Köppen:BShw; Fig. 7). Soils show some profile development and are neutral to mildly acid (pH: 6.0 - 7.0). The country rocks have an average pH value of 9.1 (Scott, 1975).

pH measurements on percussion chips* show that dilute acid solutions emanating from the oxidising pyrite-rich ore move acid-soluble copper into the country rock where it is fixed when dilution with alkaline groundwater raises the pH above the precipitation barrier for Cu. The secondary dispersion halo (defined by copper tenor \geq 10x background) enlarges the surface exploration target from 25m to 175m. Similarly, significantly anomalous copper values in the minus 140mesh fraction of the soil extend 150 m downslope of the ore outcrop, coinciding with the \geq 10x enriched bedrock zone (Fig. 8).

* See Appendix 1.

The more acid groundwater and soil conditions have resulted in considerable dispersion of copper in an otherwise alkaline system.



Figure 6. (a) : Simplified geology, (b) Annual rainfall of South West Africa (From : Scott, 1975).

The ability of an ion to remain in solution in an aqueous system (groundwater, streams) is limited by the stability of the minerals it forms by reaction with cationic species such as SO_4^{2-} , CO_3^{2-} , and CI^- . Solubilities of carbonates, chlorides, sulphates, nitrates and acetates in dilute aqueous solutions at surface pressures and temperatures are listed below (Hunt, 1972; Krauskopf, 1979; Levinson, 1974).

- Carbonates of Cr, K and Na are significantly soluble in water. Carbonates of Pb, Cd, Mn, Cu, Zn, Co, Ba, Ca, Sr, Ni, and Mg are arranged in order of increasing solubility, with MgCO₃ being sparingly soluble.
- 2. Chlorides of Sb, Ba, Rb, Sr, Cd, Ca, Co, Cu, Fe²⁺, Fe³⁺, Pb, Mg, Mn²⁺, Ni, K, Na, Sn²⁺, Sr, Zn, and Pt are all soluble in water; chlorides of Bi, Cr, Au¹⁺, Hg¹⁺ and Ag are insoluble.



1. Aggeneys

- 2. Areachap
- 3. Gamsberg
- 4. Gold anomaly
- 5. Gorob
- 6. Haib
- 7. Kantienpan prospect
- 8. Matchless
- 9. Otjihase
 - 10. Prieska
 - 11. Putsberg prospect
 - 12. Selebi-Pikwe
 - 13. Turtle Mine
 - 14. Silobela area

Figure 7. Southern Africa case history locality map showing distribution of Köppen climatic regions. (From : Carlisle, 1978).

- 3. Sulphates of Cd, Cr, Co, Fe²⁺, Mg, Mn²⁺, Ni, K, Na, Sn²⁺, Zn, and Pt are soluble in water. Those of Ba, Sr, Pb are insoluble while sulphates of Ca, Ag and Hg are sparingly soluble.
- 4. Nitrates and acetates are generally soluble except those of Pb, Ag and Hg⁺.



Figure 8. Otjihase Prospect, Traverse 500. Copper distribution in soil and rock. (From : Scott, 1975).

The above generalisations are only approximations. Nevertheless these soluble salts are formed during weathering and a consequence of their easy solubility is that they become depleted in well-drained, carbonate-free soils. In alkaline soils, they may precipitate in lower layers, mostly as carbonates or hydroxides.

Snoep and Zeegers (1979) described the Socos porphyry copper deposit in southern Peru where warm desert climatic conditions with occasional strong rainfall produced subsurface Eh and pH conditions keeping Cu in the crestal portions (of the porphyry copper) in the mobile state (Fig. 9). Precipitation occurred where this acid cupriferous groundwater flowed into recent sandy streambed alluvium with a much higher pH, producing about 1000 tons @ 3 - 5% Cu (Fig. 10).

As metal-bearing groundwaters are diluted with surface waters of high pH, or as they react with rock over or through which they flow, the pH will increase and trace metals will precipitate out as the pH of hydrolysis is reached. Hydromorphic dispersion trains in arid environments thus decay rapidly and can only be utilised in detailed follow up work.

Salts accumulate in arid and semi-arid regions, where evaporation exceeds recharge. Because of differences in their solubilities, these salts may become stratified in the soil profile. Near-surface layers of ground are wetted by rain or runoff more frequently than the deeper layers. Hence, more soluble chlorides and sulphates are illuviated from the near surface calcareous layer. Sulphates precipitate below the carbonate layer and chlorides at the wet/dry interface (Fig. 11a). This layering is reversed where groundwater evaporates from the capillary fringe, into the atmosphere (Fig. 11b ; Hunt, 1972). It can be appreciated that constant-depth soil sampling will yield false anomalies in areas of salt accumulation.

In most arid areas, the spatial pattern of soils corresponds closely to the main elements of slope and relief, with salts accumulating in topographically closed basins (playas), and in the toeslope region (Fig. 12). Enhanced soil metal values at the break in slope may thus indicate a natural concentration of soluble metals, leached from the slope soils.

The above generalisations serve as a guide only, in understanding the behaviour of metals in the secondary environment. The mobility of many elements in more alkaline solutions is governed by the formation of a wide variety of complex hydroxy- and oxy-ions (Rose, Hawkes and Webb, 1979). In particular, Cr⁶⁺, Mo⁶⁺, As⁵⁺, and V⁵⁺ commonly form complex



1.	Copiapó	70.40°W	27.40°S
2.	El Teniente	70.30°W	34.10°S
3.	Rio Blanco	70.27°W	33.15°S
4.	Socos	75.30°W	14.30°S

Figure 9. South American case history locality map showing climatic zones for Chile. (From : Baraona and Saa Vidal, 1970).



(a) Geological sketch map of Socos.
 1=granodiorites; 2=dacite porphyry; 3=granite;
 4=gossan; 5=metavolcanics; 6=quartz-silicate
 alteration; 7=limits of propylitic alteration;
 8=old workings; 9=drainage.



 (b) Cross-section through mineralisation zone of Socos showing Cu low in the central part. 1= propylitic granodiorite; 2=quartz-sericite altered granite.

Figure 10. (From : Snoep and Zeegers, 1979).

ions. For the majority of metals, the formation of complex ions increases the pH of hydrolysis and thus, the values of the Ph of hydroxide precipitation given in Fig. 5 are of limited significance in assessing geochemical migration in alkaline (arid) solutions (Beus and Grigorian, 1975). If the pH of hydrolysis of the complex is exceeded, it dissociates and precipitation takes place in the presence of such precipitating agents as S^{2-} or OO_3^{2-} , and to a lesser extent, PO_4^{3-} and SO_4^{2-} (op cit.).



Figure 11. (a) Sketch showing salt distribution in an arid environment resulting from downward illuviation, the more soluble salts being leached out of the most frequently wetted zone and precipitated in order of increasing solubility down the profile.

(b) Reversal of salt distribution in soil profile where evaporation from near surface water table exceeds precipitation. (From : Hunt, 1972).



Figure 12. Soils of the Kufra Basin in relation to geomorphic position. (From : Atkinson and Waugh, 1979).

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An interesting study of the mobility of Cu and Mo in the supergene environment was carried out by Hansuld (1967). Investigating the stability relations in a simple chalcocite-water system, Hansuld showed that Cu²⁺ is mobile in acid soils overlying oxidising poprhyry copper deposits, and is leached downslope where mixing with the normal arid environment alkaline surface waters causes precipitation of the metastable copper hydroxide, when the pH exceeds 6 (Fig. 13a). At a pH of 6, the solubility of copper is less than 3 ppb (Fig. 13a; cf Fig. 5). Similar studies on the molybdenite-water system showed that in the acid soils mantling weathering porphyry copper deposits (at $pH \leq 6$), the acid molybdate anion is relatively insoluble. However, at pH values in excess of 6, molybdenum becomes progressively more mobile as the molybdate anion (Fig. 13b). Relative mobilities are depicted schematically by arrows at the top of the diagram. This study demonstrates clearly why Mo is a pathfinder for porphyry copper mineralisation (containing Cu and Mo) in regional and follow up stream sediment surveys in arid environments.

Adsorption of trace elements onto finely dispersed suspensions of clays, and hydroxides of iron and manganese. can play an important role in the migration and precipitation of trace metals in rivers, and gossan and laterite profiles. The use of partial extractions removing only these loosely bound metals is widely used as a method of distinguishing between lithological anomalies highlighted by total extractions (XRF, hot acid leach etc.), and hydromorphic dispersions related to mineralisation. Weathering in arid and semi-arid environments forms negligible amounts of clays, and the violence of most desert rainstorms results in rapid mechanical erosion. Particles in streams are abraded to clay-sized fractions. Exposure of these particles to flood waters is generally too brief for significant dissolution and reprecipitation. The clay-sized fraction thus consists predominantly of partially weathered rock flour rather than hydromorphic precipitates (Lovering and McCarthy, 1978).



- Figure 13. Application of Eh-pH diagrams to an understanding of the relative mobilities of copper and molybdenum in the search for porphyry copper deposits.
 - (a) Some stability relations in the chalcocitewater system.
 - (b) Some stability relations in the molybdenitewater system.
 (T = 25°C : P = 1 atm.)
 - (From : Levinson, 1974; after Hansuld, 1967).

In certain desert areas, dilution of the fines by aeolian-transported silt - and clay - sized material may suppress anomaly contrast. This is not considered a problem in the Basin and Range province of the USA (Chaffee, 1975), but in the desert areas of the Near-East, wind-carried dust (minus 80-mesh fraction) has been found to be an important dilutive factor (Bradshaw and Thomson, 1979a). For these reasons, extraction schemes designed to separate hydromorphic components do not produce the same results in arid and semi-arid environments as they do in humid and subhumid areas.

Rattingan *et al.*, 1977, report on the results of a stream sediment survey over shallow copper mineralisation in the Stuart Shelf area, central South Australia. The climate is warm to hot and semi-arid (Fig.76). Drainage is internal and streams ephemeral. Fine wind-borne material in the drainages is not always clearly distinguishable from

fluvial sediment. Orientation showed that the minus 60-mesh fraction yielded higher absolute Cu values and better contrast when samples were collected shortly after rainfall when windborne material had been flushed along channels, compared with samples taken in dry periods. The authors concluded that the acid rain water lowered the pH sufficiently to release Cu into solution from the alkaline source sediment and permit sorption of ions on the newly deposited silty fraction. Analysis was carried out by atomic absorption spectrophotometry after a one hour hot concentrated perchloric acid digestion. The hot acid leach used, however, gives a near total analysis (Fletcher, 1981), and need not necessarily represent the hydromorphic component of the dispersion train. The enhanced contrast may merely be a reflection of the removal of the aeolian dilutant by the stream water.

This study shows that meaningful geochemical data can be obtained in adverse situations if careful orientation studies are carried out.

Clastic Dispersion

Residual dispersion halos always contain clastic disintegration products of the mineral deposit and its primary geochemical halos (Beus and Grigorian, 1975), especially in arid and semi-arid areas where chemical weathering is subordinate. Dispersion rates are controlled by relief, the more rugged the terrain, the more effective the role of mechanical dispersion.

Exploration techniques relying on tracing anomalous clastic dispersion trains back to source will be most successful in areas of moderate to high relief where the relationship between the heavy mineral fraction in stream sediment or overburden and its source may be established by unravelling the landscape-geochemical environment of the catchment area. In more mature landscapes dispersion trains are generally too diluted with wind-blown sand, barren alluvium, and reworked older gravels. Trace metals within clastic dispersion halos in talus, alluvium and soil are contained in one of several ways (Rose, 1975) :

- as a major element in a trace mineral, (Pb in galena, Zn in sphalerite or gahnite, U in monazite, etc),
- (2) as trace constituents in primary rock-forming minerals,(Zn in magnetite, Pb in K-feldspar, Cu in biotite),
- (3) as trace constituents in minerals formed during weathering, (Zn in octahedral sites of montmorillonite, Cu, Pb, Zn in manganese-rich fracture coatings, Pb in anglesite, Cu in chrysocolla).

An example of clastic dispersion of copper in an alkaline environment is given by Lovering *et al.* (1950) who studied the weathering and erosion of the San Manuel copper deposit, Arizona (Fig. 15). They showed that chalcocite and chrysocolla from the oxidised zone is disintegrated mechanically in the present alkaline semi-arid environment, and reports in the fine fraction (minus 70-mesh) of the soil. Slope wash carries the copper along with other soil materials into the nearby washes, where they are incorporated in the alluvium and swept downstream during floods. The downstream dispersion length depends on the amount of dilution and not chemical dissolution.

Detection of anomalous dispersions relies on our ability to isolate and enhance that portion of the chemical variability attributable to mineralisation, from background variations related to changes in bedrock lithologies.

Brown (1970) discusses the problem of particle sparsity in stream sediments in areas where weathering is strongly mechanical and shows that the likelihood of detecting the mineralisation is minimal. He studied a small drainage basin (\sim 1.6 km²) in which a quartz vein with 4% argentiferous galena outcrops over 100 m². He shows that erosion yields 37 g of galena along with 200 million grammes of waste annually. In view of the relative softness and ease of cleavage, all the galena was assumed to be in the minus 80-mesh fraction. Brown (1970) calculated that the *a priori* probability of getting one

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grain of galena in a 1g sample is less than 1:50 million. Even if we did get one grain of galena, it would only contribute an extra 13 ppm, which is less than the average lead content of feldspars (Lovering, 1976).

A similar study was carried out by Harris (1982) who, investigated clastic dispersion trains of gold. He concluded that if the gold tenor of the sediment sampled was 500 ppb (background value is 5 ppb), ignoring all questions of grain size and specific gravity, then the chance of finding one grain of gold in a 200 g sample was about 1:200. Should this in fact happen, the gold concentration in the sample would be 200 times higher than the true overall concentration. Two of Hariss' suggested methods of increasing reliability of gold geochemistry are applicable to clastic dispersion prospecting in general :

- samples should be collected from natural heavy mineral traps (eddy deposits, heads of longitudinal and point bars, etc.), and
- (2) preparation of heavy mineral separations to enhance anomaly contrast.

Heavy mineral concentrations can be used on a regional scale to mechanically eliminate the effects of dilution by rock-forming minerals. The large initial sample size (2 - 10)litres) reduces sampling error and the great concentration factor, usually several orders of magnitude, before analysis, often brings the level of some of the rarer or analytically more difficult elements within easy reach of the analyst (Meyer *et al.*, 1979).

Heavy mineral concentrates are difficult to prepare but are invaluable in arid environment geochemistry. Several schemes illustrating heavy mineral separation and analytical procedures have been published. All involve mechanical preconcentration and magnetic separation, followed by visual and chemical analysis. Methods involving analysis of magnetic and nonmagnetic fractions are detailed by Callhan (1981), Stendal (1978), and Zantop and Nespereira (1979). More detailed analysis of isodynamically separated magnetic fractions are given by Brundin and Bergström (1977) Meyer *et al.*, (1979) and Hallenstein *et al.*,(1981).

Chemical investigations on heavy mineral subfractions (based on differences in density and magnetic properties) often permit the identification of several dispersion trends for a single element either in the primary or secondary dispersion of the elements. Panned concentrate anomalies generally may be ascribed to one or more of the following groups (Basham *et al.*, 1977) :

- minerals, both primary and secondary, in which the element is essential to the composition and which can often be related, directly or indirectly, to mineralisation,
- (2) minerals, present in relative abundance, that contain the element as a non-essential trace constituent within the lattice,
- (3) altered mineral or rock fragments, oxides or hydroxides of iron and manganese or organic matter, which may have absorbed the metal, and
- (4) contamination by industrial waste etc.

Meyer *et al.*, (1979, p. 413) quote an example from south western New Mexico (Fig. 15) where panned concentrates were split into three fractions using a Frantz Isodynamic Separator: (1) minerals magnetic at 0.2 amp,

- (2) minerals magnetic between 0.2 and 1 amp, and
- (3) the non-magnetic fraction at 1 amp.

The latter fraction contains most of the common sulphide minerals of the area while the second fraction contains iron and manganese oxides precipitated from supergene solutions beyond the immediate environs of the deposits. Anomaly contrast is best in the non-magnetic fraction.

A water-conserving method of obtaining panned concentrates in arid environments is briefly described by Bugrov (1974). In interpreting panned concentrate results it is important to bear in mind that the rate at which a mineral is panned away is a function of its density, particle size, shape and wettability. The inherent hydrophobicity of molybdenite may preclude it from reporting in the concentrate. Multi-element analysis of stream concentrate bears little resemblence to that of the source from which it was derived. For multielement (XRF) results of concentrates to be meaningful and comparable, the procedure outlined in Appendix 2 is recommended.

Biological Dispersion

Elements released to groundwater during chemical weathering of rocks and derived soils are accumulated to varying degrees by plants. Element concentrations may exceed the tolerance level of certain species and hence near-surface orebodies are frequently delineated by anomalous plant communities composed of tolerant species. Toxicity of elements to plants may result in characteristic morphological changes.

Geobotany involves the visual recognition of anomalies in plant communities and morphology and their possible relation to mineralisation. The literature abounds with geobotanical case studies over known base-metal occurrences but ore discoveries directly attributable to geobotany appear to be restricted to the use of selenium indicators in discovering sandstone-hosted uranium ores of the Colorado Plateau (Brooks, 1979).

O'Kiep geologists report two local copper indicators, Ursina cakilefolia and Polymita albiflora that thrive on copper-rich soil over subcropping malachite-stained noritoids (P. Wipplinger, pers comm., 1982). In all cases, this association was noted after discovering the noritoid by more conventional methods. For a listing of the more common indicator plants, the reader is referred to Brooks (1979).

Biogeochemistry involves the collection and analysis of whole plants or selected parts of plants. In arid and semiarid environments, where the water table tends to be deep, only phreatophytes (those that obtain their moisture from below the capillary fringe), are suitable for sampling (Brooks, 1972). Mesquite (*Prosopis juliflora*) has been the most widely used phreatophyte in biogeochemical surveys in the arid regions of the western United States (Chaffee, 1975). A live root, tentatively identified as being from a mesquite plant, was collected in the Mission Mine open pit in Southern Arizona at a depth of 53m, about 20 m above the watertable (Phillips, 1963). In the arid Colorado Plateau, live juniper (*Juniperus monosperma*) roots have been observed at depths of 100 m (Cannon and Starrett, 1956).

Brooks (1972) emphasizes that there are probably up to 20 variables which can affect elemental accumulation by vegetation, the most important of which are listed in Fig. 14.

Factor	Relative importance	Method of reducing effect
Type of plant	Very great	Selection of plants by orientation survey
Organ sampled	Great	Selection of organ by orientation survey
Age of organ	Significant	Selection by orientation survey
Root depth	Significant	Use of ratios of two elemental concentra- tions in same sample
pН	Fairly significant	Selection of elemental ratios of pair of elements of same availability over pH range encountered
Health of plant	Fairly significant	Select healthy specimens only
Drainage	Fairly significant	Avoid poorly drained areas where pos- sible; also use elemental ratios
Availability of element	Fairly significant	Use elemental ratios with both elements of same availability
Antagonism of other elements	Minor	None
Rainfall	Minor	Carry out work over short period
Variable shading	Minor	Avoid shady sites if possible or use ele- mental ratios
Temperature of soil	Minor	Carry out work over short period

Figure 14. Factors affecting elemental uptake by plants and methods of reducing their effect. (From : Brooks, 1972).

The main disadvantage of the technique is its variability, caused by factors difficult to control, while the greatest single advantage of the biogeochemical technique is its penetrating power (op cit.). It is therefore suggested that in areas of relatively thin overburden, the usual geochemical techniques be applied. Biogeochemical sampling of phreatophytes may prove fruitful in areas of thick transported overburden, where normal soil and stream sediment sampling will not reflect bedrock geochemistry, but where deep-rooted plants may be drawing nutrient from bedrock.

An example of prospecting in areas of transported over-

burden where surficial soils do not reflect bedrock chemistry is provided by Chaffee and Hessin (1971). The unexploited porphyry Cu-Mo deposit, outlined by diamond drilling, is situated in an area of moderate relief (120m), and is nearly entirely buried by up to 75m of post-mineralisation desert pediment alluvium flanking the Vekol Mountains in the Basin and Range Province, southern Arizona. The climate is warm to very hot and arid (Köppen : BWhs, Fig. 15).

About 2400 samples of soils (minus 60-mesh from 5 - 15cm depth), rocks, as well as leaves and stems from two phreatophytes (ironwood and foothill palo-verde) and a xerophyte (creosote) were collected and analysed for Cu, Zn, Mn and Mo by wet chemical methods. The soil anomalies for Cu, and to a lesser extent Mn coincide with poorly metallised quartzite and do not correlate spatially with the concealed portions of the deposit. Zinc soil patterns are displaced downslope from mineralised outcrop showing zinc to be much more mobile than copper in the calcrete-covered slopes just below the outcrops.

Chaffee and Hessin (1971) describe two types of biogeochemical anomalies in areas of postmineralisation alluvium, not revealed by soil sampling. The first type, the groundwater anomaly, forms in areas where water table depth does not exceed plant root depth (\sim 30m). This is illustrated by the wider distribution of zinc in ironwood ash of plants growing along major drainages as compared with zinc in soils (Fig. 16). The authors suggest that plots of Zn in ironwood ash of plants growing in or near active dry streams, may be a reconnaissance exploration method in the search for buried base-metal deposits on desert pediments.

The second type, the bedrock anomaly, relates to areas where plants growing in barren alluvium are rooted in or near mineralised bedrock. The authors record anomalous concentrations of Zn, Cu and Mo (but not Mn) in the ash of all three plant species, growing in the pediment gravels, as much as 240 meters beyond any significant soil anomaly. The example illustrates the advantage of biogeochemical prospecting in areas of transported overburden.



- 1. Antler Peak area
- 2. Binghampton
- 3. Death Valley
- 4. Edna Mountains
- 5. Johnson Camp
- 6. Lone Star district
- 7. Majuba Hill
- 8. Meyer et al. example
- 9. North Bell
- 10. Northern Sonora
- 11. Old Dick
- 12. Patagonian Mountains

- 13. Peninsula Range
- 14. Pima district
 - 15. Ray
 - 16. Roach Lake
 - 17. Robinson Mining dist.
 - 18. Saddle prospect
 - 19. San Manuel
- 20. Searles Lake
- 21. Sheephead
- 22. Usery Mountain-Pass
- 23. Vekol
- 24. Wirepatch

Figure 15. Western USA case history locality map showing distribution of Köppen climatic regions. (From : Carlisle, 1978).



Figure 16. (a) Distribution of zinc anomalies in soil



Figure 16. (b) Distribution of zinc anomalies in ironwoodstem ash (From : Chaffee and Hessin, 1971).

The Primary Environment

Nearly all the deposits discovered to date by geochemical methods were indicated and pinpointed by secondary dispersion halos or trains in drainage sediments, waters, soils or vegetation. The vast areas of exposure in the mountain and basin deserts, where soils and stream sediments are poorly developed, lend themselves to lithogeochemical methods. The technique relates geochemical patterns in unweathered bedrock to mineralisation. Successful application of lithogeochemistry in the recognition of primary geochemical halos was pioneered by the Russians. Good reviews of the Russian literature are provided by Beus and Grigorian (1975), and Grigorian (1974). More refined techniques have been developed to interpret ore potential and define specific drilling targets, Lyakhovich, (1978), Skublov and Belonin (1981).

Govett and Nichol (1979) and Boyle (1982 a, b) have reviewed geochemical patterns in fresh bedrock denoting proximity to mineralisation. Since lithogeochemical methods apply to fresh rock samples, survey parameters are the same for all climatic environments and will not be enlarged on here. Case studies will be cited where the detection of primary halos played an important role in ore discovery.
EXPLORATION IN AREAS OF HIGH RELIEF

Secondary dispersion halos are terrain sensitive and hence an understanding of landscape processes is vital in interpreting secondary geochemical patterns. The basic desert profile comprises a mountain area and a piedmont plain (Fig. 17a) and may be subdivided on the basis of slope or relief into mountain, pediment, and alluvial plain (Fig. 17b & 18). Each physiographic setting is characterised by specific surface processes and landforms which dictate the geochemical exploration approach.

Desert landforms result from the interaction between bedrock geology and erosional processes and hence many characteristic landforms may evolve in any physiographic setting. Flat-topped mountains, which often represent remnants of older erosion surfaces (mesas), have soils with well developed B (clay) horizons in contrast to the shallow rocky soils prevalent in desert mountain lands (Dregne, 1976). As these soils frequently formed in more humid paleoclimates and are of limited areal extent in highly dissected rugged terrain, they are not considered suitable sampling media.

Several landforms make up the mountain front. In areas where summit rounding is ineffective, resistant cap rocks form steep cliff faces. Rounded upper slopes characterise hills where exfoliation is dominant. In both cases erosion is gravity controlled with dislodged rock fragments or blocks accumulating on and at the base of the gravity slope as a talus or scree slope (Fig. 18). Talus slopes with sparse debris mantles occur where caprock is compact and poorly jointed and are subject to granular disintegration. Slopes receiving waste from mountain summits formed by thick, well jointed caprocks may be completely rubble-covered, especially where the debris is erosion resistant. Commonly the cliffs supply only part of the debris slope rubble. Much of the mantle lower on the desert debris slopes is derived from the underlying rock itself. Slow downslope mass movement of the talus mantle is common in cold deserts where slopes are subjected to the action of periodic frost and thaw. Talus creep is the major surface process on cold slopes underlain by argillites. In hot deserts, slow mass movement on slopes is relatively unimportant. Here accumu-



Figure 17. Components and morphometric properties of the characteristic desert profile. (From : Cooke and Warren, 1973).



Figure 18. The major landforms associated with arid and semi-arid regions. (From : Pritchard, 1979).

lated debris tends to weather *in situ* by comminution. Fines are removed by slope wash (Mabbutt, 1977). Anomalous geochemical trends in talus fines thus tend to be displaced less in the downslope direction in hot deserts than in colder desert areas.

Runoff is high on arid slopes due to the lack of vegetation and sediment cover. Because of the predominance of wash transport over mass movement on hillslopes, low order channels receive most of their load in dimensions they can transport. Hence stream beds are in or close to bedrock with gravel-and sand- sized sediment the most abundant. Debris slopes normally lead smoothly to the channel. Canyons in a desert upland of strong relief consist of a narrow gravelly or sandy floor from which the hillslope rises directly, locally as cliffs and more commonly as debris slopes.

Areas of high relief, under any climatic regime, are characterised by a high drainage density. There is also a strong positive correlation between drainage density or channel frequency and aridity as well as consequent areal extent of rock exposure (Fig. 19). The two most commonly used exploration methods applied in arid uplands are therefore, lithogeochemistry and stream sediment geochemistry.

Lithogeochemistry

Rock exposures are generally unweathered with minimal oxidation, thus exposing primary dispersion halos in their pristine state. In the arid Basin and Range Province (western USA), the majority of geochemical exploration surveys that have been conducted have utilised outcrop sampling, either alone or in combination with other media.

Fresh and Altered Rock Samples

Trace element contents of scattered samples collected in granitic terrain enables discrimination between productive and barren intrusions on a regional scale. This is especially true of tin which generally, but not universally, shows enrichment in intrusions associated with mineralisation (15 - 30 ppm Sn), compared to 5 ppm Sn or less in barren or non-productive granite plutons (Beus and Grigorian, 1975; Juniper and Kleeman, 1979).



Figure 19. A: Variations of drainage density with aridity in the southwestern United States. Each point represents one basin.

B: Variation of channel frequency with percentage of background in southwestern United States. (From : Mabbutt, 1977).

Randal (1975) combined lithogeochemistry and geological mapping in giving a preliminary understanding of a zone of alteration coincident with Cu-Mo mineralisation in previously unmapped terrain, in the deeply dissected western edge of the Sierra Madre Occidental, Mexico. The region is enriched in tin with ignimbrites and granites averaging well over 50 ppm and locally exceeding 100 ppm Sn. Rocks were collected at trigonometric beacons, claim corners, and over known mineralisation and assayed for Sn, Mo and Cu by atomic absorption. Results define a multi-stage intrusion with a core of molybdenum enrichment (100 - 350 ppm Mo) partly surrounded by a coincident copper-tin zone with whole rock tin values ranging from 50 to in excess of 250 ppm Sn. Background averages 25 - 40 ppm Sn. Tin content of whole rock samples thus clearly outlined a zone with Cu-Mo potential, in a high tin background area.

In areas of shallow residual soils, C-zone samples may give enhanced tin values. At the Majuba Hill Cu-Mo-Sn-Ag porphyry deposit (Fig. 15), Pershing County, Nevada, tin concentrations in the plus 30-mesh fraction of the C-zone (15 - 125 ppm) are higher than in the underlying rocks which average 10 - 20 ppm (Bookstrom and MacKenzie, 1978; Trites and Thurston, 1958). Cassiterite grains are believed to be residually concentrated in the C-zone during soil profile development.

Surface concentrations of cassiterite in small bedrock depressions may form by the winnowing action of wind in hot deserts on mineralised, and on barren granites. Abundant cassiterite in elluvium and colluvium need not indicate mineralisation but should be followed up by whole rock analysis (Bugrov, 1974).

Major element distributions in primary enveloping halos of porphyry copper intrusions are extensively documented in the literature. Exploration and evaluation is based on the recognition of trace and major element trends characterising the various alteration halos. The deposits occur in a diversity of host rocks and successive alteration zones may overlap, interfinger or be telescoped. The surface geochemical expression of the primary dispersion halo may be altered by acid leaching associated with oxidation of pyrite. Nevertheless, there are certain major and trace element trends and ratios that are useful in exploration in arid environments :

Boyle (1982a) lists three significant changes in major element content on approaching porphyry-type mineralisation :

- (a) an increase in K and a decrease in Na and Ca resulting in an increase in the $K_2 O/Na_2 O$ and $K_2 O/CaO$ ratios
- (b) a consistent decrease in the $SiO_2/total$ volatile content ratio and,
- (c) a decrease in Ca, Mg and Mn and a consequent increase in Al_2O_3/CaO ratio.

Since rubidium-potassium and strontium-calcium behave sympathetically during hydrothermal alteration, an increase

in the Rb/Sr ratio should indicate proximity to porphyry mineralisation (Plimer and Elliott, 1979). Reasons for studying the rubidium and strontium variations in preference to potassium and calcium include :

(1) greater sensitivity to hydrothermal processes, expressed as variations of the K/Rb and Ca/Sr ratios ; (2) wider ranges of variation than major elements ; (3) more readily amenable to rapid and precise analytical determination. Oyarzun (1975) studied the behaviour of Rb and Sr if alteration zones were superimposed on different rock types.

Where porphyry copper mineralisation intrudes andesitic rocks (Rio Blanco, El Teniente, Fig. 9), rubidium is consistently enriched by a factor of 2 - 4 times in the propylitic and potassic alteration zones (Fig. 20). Strontium is strongly depleted in the Rio Blanco potassic alteration zone, but not significantly so at El Teniente, where it appears to be locked up in abundant anhydrite.

	Rb (ppm)	K/Rb	Sr (ppm)	Ca/Sr
Fresh andesite	50	330	480	77
Rio Blanco potassic	155	335	60	35
El Teniente				
propylitic	105	167	338	
potassic	195	160	380	
leached cap	194		27	

Figure 20. Rubidium - strontium and potassium-calcium variation in altered rocks adjacent to porphyry copper mineralisation. (From : Oyarzun, 1975).

The immobility of Rb during weathering (Fig. 20) may be useful where weathering has masked the mineralogical effects of hydrothermal alteration.

In a study of the Wirepatch porphyry molydenum prospect, Colorado (Fig. 15), Pride *et al.*, (1979) confirmed the strong depletions of strontium, calcium and sodium and the stability of rubidium and potassium in the weathered zone and conclude that rubidium is the best indicator of alteration. As rubidium enrichment is restricted to the alteration zones its use in regional surveys is limited. In porphyry deposits that are intruded by high rubidium-bearing granitoids, no significant rubidium anomalies result due to lack of chemical contrast between intrusive and intruded rocks (Oyarzun, 1975).

Pathfinder elements may be used in conjunction with major elements to localise primary dispersion halos. The use of thallium as a guide to mineralisation has recently been suggested by Ikramuddin et al., (1982) who demonstrated that the ratios K/Tl and Tl/Sr may be better quides to mineralisation of hydrothermal origin than K/Rb and Rb/Sr ratios. The volatile trace element tellurium occurs in alteration halos enveloping porphyry-type deposits and polymetallic vein deposits and forms wider primary dispersion halos than the major elements. This, coupled with its immobility in the secondary environment, where it has an affinity for ferruginous oxidation products, may be used in regional exploration to outline areas of interest, (Watterson et al., 1977).

The tellurium anomaly associated with the disseminated porphyry copper deposits of the Robinson mining district, Nevada (Fig. 15), is shown in Fig. 21. The deposits are related to quartz monzonite stocks which outcrop in mountainous terrain of the Basin and Range Province. Extensive surface leaching, attributed to a more humid paleoclimate, has resulted in the fixation of Te in oxidised iron sulphides. The areal extent and magnitude of the anomaly are impressive, but Watterson *et al.*, (1977) point out that the analytical technique needs refining.

It should be remembered that lithogeochemistry is an effective tool only when the geochemical changes brought about by the mineralising event can be clearly distinguished from chemical patterns related to petrogenesis, metamorphism, and weathering. The examples cited are from the rugged terrains of arid areas where exposures are abundant, and the subtle chemical variations may be readily related to some clearly observable geological change. Usually, in areas of good exposure, lithogeochemistry is overshadowed by stream sediment



Figure 21. Relationship between tellurium distribution (ppb) of rocks and porphyry mineralisation, Robinson district, Nevada. (After : Watterson et al., 1977).

sampling, careful geological observation, and geophysical methods.

Stream Sediment Geochemistry

Upland desert drainage forms a system of connected, closely branching washes with clean-scoured rocky channels in the head tracts, passing down-valley into gravelly floors. Runoff into these channels is a function of rainfall intensity, slope roughness and absorption. Continued light rain results in low runoff yields that may not cause stream flow. Intense down pours result in runoff on gently dipping slopes that are generally mantled with fine-grained debris. Runoff on steeper slopes is limited by the hydraulic roughness and higher infiltration rate (Mabbutt, 1977). Shallow slopes tend to yield more sediment per unit area to the stream than steep slopes especially during brief showers. Mineralisation exposed on gentle slopes is thus more likely to report in the stream sediment than that exposed on scarp slopes.

Downstream clastic dispersion trains are rapidly diluted by sediment influx from neighbouring channels draining unmineralised areas (Brown, 1970). Desert storms are often highly localised and may cause a single tributary to flood while adjacent washes receive insufficient runoff to flow, and mineralised surface silt may be eroded or buried by barren alluvium. Intensity or duration of precipitation may be such that the infiltration rate of a rough-surfaced slope (with or without exposed mineralisation) is not exceeded, while an adjacent smooth slope is supplying sediment to the stream. Where samples collected from the centre of active streams in humid climates tend to reflect the average composition of the exposures in the drainage basin, in arid and semi-arid climates, situations could arise where sediment metal content is anomalously high or low, and may be derived from a small catchment within the basin.

Sand and Silt as Sampling Media

Sediments in headwater streams are poorly sorted and contain subordinate fines. Metals occur as mechanical disintegration products of primary mineral grains, secondary oxides and gossan fragments. Metal-rich groundwaters do not normally come into contact with stream sediments in arid terrains, hence, dispersion trains are better defined by total than partial extraction techniques (Chaffee, 1975). Analysis of a coarse and fine fraction is recommended by Levinson (1980): total analysis (XRF) of a coarse fraction (minus 4 to plus 16or minus 10 to plus 30-mesh) which concentrates gossan fragments, and cold extraction on the minus 80-mesh fraction to define any hydromorphic dispersion.

In the Basin and Range Province, western USA, the siltsized fraction of stream sediment is used in preference to sand-sized material (Lovering and McCarthy, Jr., 1978) as it yields longer dispersion trains than the coarser fraction. The authors stress that chemical dispersion is minimal and that most base metals report in the fine rather than the coarser fraction due to the friable nature of supergene ore minerals and associated iron oxides. The sand-sized fraction is more suitable for determination of abrasionresistant minerals such as chromite, cassiterite, monazite, wolframite, scheelite, columbite, tantalite and fragments of Au-bearing quartz.

The suitability of various *size fractions* and *strengths* of chemical attack in very arid environments is discussed by Bugrov (1974). The area studied forms part of the highly dissected stony Eastern Desert of Egypt (Fig. 22). In an orientation survey, samples collected from wadi (dry stream bed) alluvium downstream of outcropping copper mineralisation, were split into six size fractions and copper determined by wet (cold biquinoline) analysis as well as by spectrographic methods. The data (Fig. 23) show that anomalous dispersion trains are of equal lengths (3.5km) for both extraction techniques and that 93% of spectrographic anomalies are in the minus 1 - plus 0.25mm fraction, while 73% of cxCu is in the minus 0.25mm fraction. The ratio total Cu/cxCu varies from 20/1 to 5.5/1 (in anomalous concentrations) showing copper dispersion to be largely mechanical.



Figure 22. The Köppen climatic zones of North Africa, see Fig. 2 for symbol descriptions. (After : Walton, 1969). 1. Bugrov (1974) study area. 2. Blain (1978) study area. 3. Ayalon (1976) study area).

Fraction (mm)	Background (p.p.m.)		Anomalous content (p.p.m.)		No. of anomalous samples		
	Cu	CxCu	Cu	CxCu		Cu	CxCu
inus 1-plus 0.75	31	1.9	100	5.2	_	14	3
minus 0.75-plus 0.5	30	2.1	96	6.0		12	4
ninus 0.5-plus 0.25	29	2.5	95	7.0	14	11	4
ninus 0.25-plus 0.15	27	2.8	66	7.6		3	4
minus 0.15-plus 0.075	20	3.2	62	8.0		0	9
minus 0.075	18	3.5	51	8.9		0	16

Figure 23.

Summary tabulation of background, and anomalous $(\bar{x} + 350)$ values for Cu and cxCu in six size fractions and distribution of anomalous results of 60 sediment samples, Darhib, Eastern Desert, Egypt. (From : Bugrov, 1974).

Bugrov (1974) concludes that total analysis of the minus 1-plus 0.25mm fraction is the most reliable technique in copper prospecting using wadi alluvium. This fraction also eliminates windblown sand which generally reports in the minus 60-mesh fraction. The use of the cxCu/Cu ratio in stream sediments has been successfully applied in tropical and temperate terrains for the recognition and interpretation of hydromorphic anomalies and distinguishing them from mechanically-derived dispersion trains. (Coope (1973), points out that caution in the use of cold extractable copper (cxCu) is required in areas of acidic ground and stream water near oxidising pyrite where the cxCu/Cu ratio tends to be depressed due to increased mobility of copper. In neutral to alkaline sediments the method works well (op cit.).

The study by Chaffee *et al.*, (1981) over a deeply buried porphyry copper (but with fresh pyrite and supergene copper outcropping) in the Patagonian Mountains, Arizona (Fig. 15), discusses the use of the copper ratio in aridterrains. Cold extractable copper (cxCu) was determined using the Cu-specific reagent 2,2'-biquinoline after a 30 second sample digestion in 6M HCl. The porphyry is clearly outlined by spectrographic analysis on the minus 60-mesh fraction of stream sediments. Plots of cxCu/Cu at varous thresholds yield no new information that could not be readily obtained using either partial or total extractable copper. There is no consistent correlation of sites of low ratio values to areas of pyrite and Chaffee *et al.*, (1981) conclude, as suggested by Levinson (1974, p.360), that the copper ratioing technique does not provide meaningful information in arid environments.

Sequential partial dissolution of specific mineral phases provides information on the partitioning of metals among hydromorphic and detrital components within samples and hence on factors influencing their dispersion. The practise should form part of any orientation survey to determine the appropriate extraction that best isolates that portion of the sample metal content reflecting mineralisation, thus enhancing anomaly contrast. Bradshaw et al., (1974) reported that the strength of metal bonding varied significantly among different temperate and tropical environments. In a recent study, Filipek and Theobald (1981) investigated the factors influencing the partitioning of Cu, Pb, Zn, Mn and Fe in samples of stream sediment and in rock with supergene iron oxide coatings from a zone of porphyry copper mineralisation in an arid to semi-arid environment - the North Bell area near Tucson, Arizona (Fig. 15).

Samples of the minus 80-mesh fraction of stream sediment, fracture coated rock, as well as samples of jarosite and chrysocolla, scraped off outcrops, were subjected to a series of extractions in a scheme (Fig. 24) originally designed for use on samples from humid sub-tropical climates. The fractions that can be effectively separated are shown on Fig. 24.

The sequential extraction results on sediments show that immediately downstream of the strongly leached gossan cap overlying the supergene chalcocite zone, the 1M-acetic acid (HOAc) extraction for Cu, Zn and Pb yields very high contrast anomalies with short dispersion trains, indicating hydromorphic transport close to the mineralised zone. The residual fraction yields much longer downstream dispersion trains of Cu, Pb and Zn, but with lower contrast, pointing to the clastic nature of metal dispersion in this semi-arid environment. Total analysis of sediment is thus suggested in regional work and an acetic acid leach for detailed followed up.



Figure 24. Sequential extraction procedure for determining chemical fractionation of the sediment and outcrop samples. Attacks used : Acetic acid (HOAc); cold hydroxylamine hydrochloride (C-Hxl); hydrogen peroxide (H_2O_2); hot hydroxylamine hydrochloride (H-Hxl); and the Residual. (Filipek and Theobald, 1981).

Interpretation of fracture-coated rock geochemistry is complicated by the effect of variable proportions of rock and fracture coating material from sample to sample. This may be overcome by using the total Cu/Fe ratio. In potassic rocks most of the iron reports in the H-Hxl fraction while in phyllic rocks iron (as jarosite) is mostly in the residual fraction. Potassic rocks have the highest total copper concentrations and the lowest proportion of residual copper while rocks from the phyllic zone have maximum Cu in the residual fraction. Total Cu/Fe ratios thus show maximum values within and near the potassic zone and minimum values in the phyllic zone. Cu/Fe patterns of coatings may be used in determining alteration zones.

About 80 percent of the jarosite reports in the residual fraction, the remainder in the H-Hxl extract. Zinc coprecipitates with jarosite and hydrous Fe oxides but where manganese is dominant, Zn shifts from the H-Hxl to the C-Hxl fraction suggesting competition by Mn oxides for Zn. This applies to a lesser extent to copper. Lead in all samples was below detection limit for the three milder extracts, reporting mainly in the residual and H-Hxl fractions. This shows the affinity of Pb for Fe in the weathered environment (plumbojarosite).

Manganese in all sample media is concentrated in the Mn-oxide or C-Hxl fraction. Assignment of unique phases, such as Mn oxides to a given extraction in arid environments can lead to incorrect interpretations. The dissolution of chrysocolla resulted in ten times more copper than manganese being extracted in the Mn-oxide fraction. Copper here is obviously not associated with manganese.

The above results show that dispersion in arid environments is mainly clastic with very restricted hydromorphic activity close to the gossan. The study also furnished an insight into element mobility in the weathering environment, showing manganese oxides to limit the mobility of Zn and to a lesser extent Cu and Pb, the latter being preferentially concentrated in iron oxides. Sequential analysis is thus recommended in the orientation stage, to obtain an insight into local supergene processes, to enable selection of the optimum extraction scheme, and hence permit confident data interpretation.

Stream sediment orientation studies were carried out in the drainage crossing the Haib porphyry-type copper mineralisation by Beeson and Brunke (1976). The prospect is situated in highly dissected terrain in southern Namibia (Fig. 7) and has been extensively prospected by Rio-Tinto in the 1970's. Copper mineralisation is associated with a quartzfeldspar porphyry stock intruding coeval acid to intermediate volcanics including feldspar porphyry, quartz porphyry, quartz diorite and andesite. Pyrite, chalcopyrite and secondary chalcocite are exposed at surface. Chrysocolla, sooty chalcocite, malachite and brochantite have been exploited on a limited scale from the thin oxide cap exposed in the prospect drainage (Haib Mine, Fig. 25), resulting in some downstream contamination.

Stream sediment in this arid (Köppen BWhs), rugged terrain consists of little-weathered, boulder to gravel-sized fragments of country rock, and small amounts of gossan and oxidation products ranging in size from pebbles to silt-sized rock flour. Beeson and Brunke (1976) collected 14 sediment samples along a 6-km stretch of a tributary draining the mineralised area (Fig. 25). The minus 200-mesh fraction of stream sediment was analysed for Cu, Pb, Zn, Mn, Cr, Co, Ni, and Li by atomic absorption after a nitric-hydrochloric acid leach. A panned concentrate prepared from the remaining plus 200-mesh fraction was analysed for Cu, Pb, Zn, and Mn by atomic absorption after a hydrofluoric-perchloric acid digestion (discussed later).

The minus 200-mesh fraction was chosen since Beeson et al., (1975) showed this size to give higher absolute values and better anomaly-to-background contrast than the minus 80-mesh fraction in an orientation survey across the Aggeneys and Gamsberg massive sulphide deposits.

Beeson and Brunke (1976) showed that for all the elements assayed, only copper indicated the Haib mineralisation. All samples from the tributary across the potential ore zone returned anomalous Cu values between 2 and 9 times the regional background of 47 ppm Cu (Fig. 26). Assayed copper tenor increases gradually from 100 ppm at localities 3 and 4 to a maximum of 425 ppm some 1200 m downstream of the surface oxide workings. Beeson and Brunke ascribe this increase of copper from sample 4 to sample 11 as a cumulative build up of copper





Figure 26. Copper content of the -200 mesh fraction (solid line) and heavy mineral concentrate (dashed line) of sediment in the dry stream bed draining the Haib porphyry-type mineralisation (From : Beeson and Brunke, 1976).

in sediment across the mineralised zone. From here onwards, for about 2 km, copper content remains relatively constant between 200 and 300 ppm (4 - 6 times background). The anomaly is completely swamped where the tributary enters the high-order Haib River (Fig. 26). Hence sampling of highorder drainages is of little value in regional stream sediment surveys (op cit.).

Further orientation was carried out by the author in order to establish metal content variation with sample type, mesh size and strength of chemical attack. Silt samples were collected from natural mud and silt traps on the downstream side of large boulders and bushes in the stream bed. Some of the coarser fraction immediately below the silt veneer was incorporated in the sample. Each sample comprises a composite of 5 to 10 subsamples collected from a 20 - 30 m radius. The plus 40-mesh ($425\mu m$) fraction was discarded and the remainder split into three fractions (below).

Stream gravel, collected at 15 to 20 cm depth from gravel bars in the centre of the active stream bed was split into four fractions : the plus 8-mesh fraction which was discarded, and three finer fractions for analysis (below). All samples were analysed at the Anglo American Research Laboratories by X-ray fluorescence and by atomic absorption after a two-hour leach in cold, 0.5M hydrochloric acid. The six samples sent for assay from each site are :

- 40 to + 80-mesh fraction of silt
 - 80 to + 200-mesh fraction of silt
 - 200-mesh fraction of silt
 - 8 to + 20-mesh fraction of sand-bar gravel
 - 20 to + 40-mesh fraction of sand-bar gravel
 - 40 to + 80-mesh fraction of sand-bar gravel.

Plots of X-ray fluorescence results across the mineralised zone show, in terms of absolute Cu values, that the fractions (1 to 6 above) may be arranged in the following order of descending Cu tenor : $1 \cong 6 > 2 > 3 > 5 > 4$. Plots of cxCu suggest a similar sequence : $1 > 6 \approx 2 > 4 > 3$ > 5. The minus 40 to plus 80-mesh fraction thus yields highest absolute Cu values in both total and partial analysis. Total analysis (Fig. 27) returns consistently higher results than partial analysis (Fig. 28). Since silt is uncommon, subsample 6 is recommended to maximise absolute Cu tenor in the sample.

The anomaly to background ratio for Cu was determined for samples 38 (300m downstream of the Haib prospect) and 41, some 2,6km downstream, using the average Cu values for samples 42 - 44 for a particular fraction and extraction as background. For copper determined by XRF the fractions may be arranged in the following order of descending contrast :

- (a) at locality 38 : 6 > 1 ≅ 5 > 4 > 2 > 3 (from 13.2 x background for fraction 6 to 3.8 x background for fraction 3).
- (b) at locality 41 : 1 > 6 > 2 > 5 > 4 > 3 (from 8.2 x background for fraction 1 to 4.6 x background for fraction 3).

To maximise contrast therefore the minus 40 to plus 80-mesh fraction of sandbar gravel or of silt is recommended. Again, since silt is not common, the gravel subfraction is preferable.

Similar sequences of decreasing contrast for coldextractable copper are :-

- (a) at locality 38: 6 > 5 > 4 > 2 > 1 > 3 (from 26.5 x to
 7 x background for samples 6 and 3 respectively).
- (b) at locality $41: 5 \cong 2 \cong 6 > 4 > 1 > 3$ (from 10.4 x to 7.3 x background for samples 5 and 3 respectively).

Again fraction 6, is the best sample for maximising contrast.

The orientation study suggests that in terms of anomaly detection, total or partial analysis of the minus 40 to plus 80-mesh fraction of sandbar gravels or of backwater silt



Figure 27. Comparison of total copper content of the -40 to + 80-mesh fraction of stream bar gravel with that of -200-mesh fraction of backwater silt, Haib area, Namibia. Sample locations shown on Fig. 25.



Figure 28. Comparison of cold-extractable copper content of the -40 to + 80-mesh fraction of stream bar gravel with that of the -200-mesh fraction of backwater silt.

yields comparable results. Since gravel is ubiquitous in the drainages of the study area and silt scarce, especially in the lower-order tributaries, the gravel sample is the better sample medium. In the anomalous stream (samples 29 - 41, Fig. 25) total copper content of subfraction 6 is twice cxCu while in the Haib River total Cu is just over 3 times cxCu, accounting for the high anomaly to background ratio of the partial analysis in the tributary draining the mineralisation. Exploration for further Haib-type mineralisation in this hot, arid, rugged terrain should thus utilise partial analysis of the minus 40 to plus 80-mesh fraction of sandbar gravels. To gain maximum geochemical information the multi-element XRF analysis is recommended in regional exploration in this terrain.

The consistent poor performance of the minus 200-mesh sample shows that the weak partial analysis is removing pulverised secondary copper oxides rather than hydromorphically dispersed copper. The assumption by Beeson and Brunke (1976) that results obtained by Beeson *et al.*, (1975) in the subdued piedmont terrain of Bushmanland are applicable to the strongly dissected Orange River valley area, is questioned. The study shows clearly that base-metal dispersion in similar climates is modified by terrain.

Panned Concentrates as Sampling Media

Separation of heavy minerals from stream sediments effectively removes diluting rock-forming minerals such as quartz and feldspar, and has wide applicability in arid mountainous terrain where clastic dispersion trains may be short and sediments poorly sorted. Selection of sample site is vital for results to be comparable.

Mosier and Allcott (1979) maximised the amount of heavy mineral concentrate in their samples by selecting locations in the channel where heavy sediments were naturally concentrated, often indicated by areas of black sand. This procedure may give satisfactory results in regional surveys but is not recommended for quantitative follow up work. Heavy mineral distribution in stream sediments is controlled by variations in specific gravity, hardness, grain size of source rock(s), and abrasion resistance, as well as grain settling velocities and the degree of sorting (Ayalon, 1976). These factors result in the inhomogeneous distribution of heavy minerals in the stream channel and hence the considerable differences in the relative amounts of minerals in sediment samples derived from the same source. Samples collected from surficial or buried black sand veneers may yield anomalous results that can be attributed to the degree of natural panning of the original sediment, or to the position in the stream where the sample was collected. For meaningful results, the scheme outlined in Appendix 2 is suggested.

Panned concentrates are useful in locating areas enriched in cassiterite, copper, lead, zinc, wolframite, rare earths etc. Separation into strongly magnetic and slightly magnetic fractions has been discussed.

The superior ability of panned concentrates over sediments in locating clastic dispersion trains in rugged terrain is shown by Beeson and Brunke, 1976 (Fig. 26). Mean Cu content of the panned concentrates from the stream draining the mineralised zone is 9 times regional background. Maximum value reported is 34 times background. As with the sediment exercises (Figs. 26, 27, and 28), the panned concentrate dispersion train does not persist into the higherorder stream.

Nonmagnetic panned concentrates are prepared by removing magnetite from the heavy mineral concentrate with a handmagnet. The remaining concentrate may be split up into several fractions using a magnetic separator. Exploration targets for nonmagnetic refractory minerals such as cassiterite, thorite, monazite, and most sulphides, are better defined by analysis of the nonmagnetic heavy mineral fraction than by sediment analysis.

Figure 29 compares the thorium distribution in the minus 80-mesh fraction of canyon sediments with that of non-



Figure 29. His the the

Histograms showing frequency distribution of thorium and geographic distribution of anomalous thorium in (a) -80mesh (-0,18mm) stream sediments and (b) nonmagnetic panned concentrate (at 0.6amp setting using a Frantz-Isodynamic Separator). (From : Mosier and Allcott, 1979). magnetic panned concentrates. The study area forms part of the mountainous terrain of northern Sonora, Mexico (Fig. 15), underlain by Mesozoic-Tertiary volcanics and minor sediments. The panned concentrate was collected from black sand veneers and the minus 0.18mm fraction gound to minus 0.105mm for magnetic separation by a Frantz separator at a 0.6 amp setting. Both the 0.6 amp nonmagnetic fraction and sediments were analysed by optical emission spectrography. The superiority of the nonmagnetic fraction over stream sediments can be seen from Fig. 29. Similar plots were obtained for Y and La.

Talus Sampling

Talus is composed of rock fragments of any size, derived by mechanical breakdown of cliffs and steep slopes and accumulates by gravitational falling, rolling or sliding as an outward sloping mass of debris (talus cone, apron) at the base of the mountain front slope (Figs. 17 and 30). Talus fines may be used as a sample medium in very rugged terrain where soils are not developed and stream sediments virtually absent. No mountains need be climbed as is the case with lithogeochemical prospecting, and most talus aprons and cones are readily accessible via streambeds (see : Maranzana, 1972, Fig. 1).

Talus anomalies define a smaller source area than stream sediment anomalies and hence more samples are needed per unit area. Talus fines (minus 80-mesh fraction) are equivalent to the clastic component of stream sediment but are more homogeneous in composition and more truely represent a composite sample of their source area. Results of talus surveys are superior and easier to interpret and follow up in areas where rapidly decaying dispersion trains are superimposed on backgrounds with high metal values (Hoffman, 1977 ; Maranzana, 1972).

Samples are collected from immediately above the boulder apron (Fig. 30), at regular intervals determined by the talus cone width, or target size. Several samples are

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collected from a 20m² area, composited, seived to minus 80-mesh and analysed in the same way as stream sediments. Talus aprons forming in actively dissecting arid environments will contain fresh sulphides as well as eroded oxidation products. The high infiltration rate of these rough-surfaced slopes permits oxidising rainwater to leach some of the metals as it trickles through, and along, the base of the debris mantle. Some of this metal will reprecipitate, due to evaporation, at the boulder apron break in slope. Metal content in talus fines may thus, in part reflect bedrock topography.



Figure 30. Idealised diagram of talus cones formed at the base of a cliff or steep slope. (From : Strahler, 1975).

In order to distinguish between the mechanical and hydromorphic components of slope-break anomalies, Bradshaw et al., (1978) suggest either up slope sample traversing or the use of the cold extractable metal (cxMe)/total Me ratio. A low cx/Me/total Me indicates mechanical dispersion while a high ratio suggests significant hydromorphic dispersion due to groundwater seepage No case study could be found in the literature where the cxMe/total Me ratio successfully discriminated between talus break in slope and clastic dispersion anomalies, but the reader is referred to the conclusions drawn in the Chaffee *et al.*, (1981) study (p. 43). Maranzana (1972) compares the results from talus fines (minus 80-mesh) with that of stream water and sediment from the Los Pelambres porphyry Cu-Mo deposit situated in rugged terrain some 210 km north of Santiago (Fig. 9.). The climate is semi-arid with occasional rain or snow in winter. Soil and stream sediment are virtually absent. Talus cones cover about 80 percent of the area.

Stream water and sediment are anomalous in copper over the 14 km stretch sampled downstream from the alteration zone, but background is so high that the anomalies merely point to the presence of mineralisation within the catchment area. The molybdenum dispersion train is much shorter, probably due to the low pH of the stream waters (4.8 - 5.4). The talus fines clearly outlined potassically altered areas and minor stringer mineralisation in the propylitic zone and yielded better geochemical contrast for molybdenum than the sediments.

Talus fine sampling does not surpass drainage sampling in rapid coverage of large areas. However, a combination of talus and stream sediment sampling is recommended, each complementing the other.

EXPLORATION IN AREAS OF MODERATE RELIEF

The Davisian cycle of erosion in humid areas (Fig. 31b) describes the various stages of landscape development by gradual downwearing from youth to maturity (Fig. 32b). The equivalent erosional process in the worlds arid mountain and basin deserts is shown in Fig. 31a and is primarily a result of mountain front retreat (Fig. 32a).



Figure 31. Stages in the erosion of an uplifted block-faulted mountain : (a) in arid and semi-arid environments, by slope retreat or back-wearing, resulting in the juxtaposition of terrain with rugged and subdued relief throughout most of the erosional cycle; and (b) in humid climates, by downwearing or peneplanation giving rise to a mature stage dominated by moderate relief. (After : Spencer, 1972).

The distinction between exploration geochemistry in rugged and moderate relief in humid environments is one of choice of sample media. Moderate relief brings with it a well developed podzolic soil profile which forms the basis of many of the concepts used in connection with soil surveys in geochemical exploration (Levinson, 1980). In arid areas the

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difference between landforms of rugged and moderate terrains is one of scale. Residual soils are strong and show profile excellent sample media for the development, but present detection of secondary, mechanical dispersion trains. Exposures of gossan are more abundant than in rugged terrain where active erosion mitigates against preservation. Gossan searching is thus an important exploration technique in areas of moderate relief. The greater maturity of the landscape and resulting complexity of landforms necessitates constant terrain evaluation so as to optimise the exploration approach. Exploration techniques useful in arid areas of rugged relief apply equally well to areas of moderate relief, but our discussion will concentrate on exploration techniques not covered in the previous section.



(a)

(b)

Figure 32. Composite diagram representing valley-side profiles at successive stages in an ideal erosion cycle in (a) : arid and semi-arid environment, and (b) : in a humid cycle. (After : Holmes, 1955).

Soil Geochemistry

Soil profiles are not usually developed in the hilly Basin and Range Province (Chaffee, 1975). The shortage of moisture restricts weathering and plant growth, as a result desert soils forming on the lower, flatter slopes are thin, alkaline, and stony with indistinct profiles. Soils are characterised by abundant partly weathered fragments of bedrock (grus). Such skeletal soils, known as lithosols, are maintained in a juvenile state of development by active erosion (Fig. 33). In hot dry hilly areas (Köppen, BW), lithosols are the commonest soil type. Their metal composition may correspond quite closely to that of the underlying parent material (Lovering and McCarthy, 1978), and hence most soil surveys are based either on the analysis of the economic metals being sought (ore metals), or associated pathfinder elements if their behaviour in the secondary environment results in more distinctive or significant dispersion patterns.



Figure 33. Diagrammatic representation of soil profiles. (a) Typical soil profile. (b) Climatic variations. (From : Brooks, 1972).

Base Metal Dispersion in Soils

On steeper slopes, some downslope displacement of anomalies occurs due to soil creep (Lovering and McCarthy, 1978), or slope wash. The anomaly peak generally coincides with the bedrock source however, since soils are thin and dispersion is mainly mechanical. This is clearly shown by a soil survey conducted over the Collins East Vein, Pinal County, Arizona. The climate is hot and arid (Köppen, BWhs). The siliceous vein hosts commercial grade Pb, Mo, V, Cu and some gold. Soil is rocky, iron-stained, of highly variable thickness and intermixed with large talus blocks. The peak of the soil Pb anomaly coincides with the subcropping vein. Downslope displacement is evident (Huff, 1952) and provides a larger exploration target (Fig. 34).



Figure 34. Relationship between Collins East vein, Mammoth St. Anthony mine, Pinal County, Ariz., and geochemical anomaly in residual soil. (From : Huff, 1952)

The nature of the displaced halo depends on slope processes, soil pH, depth of weathering and mobility of the elements eroded from the mineralised zone. The resulting dispersion halo may give a false impression of the metal tenor in the underlying mineralisation. This is well illustrated by a soil survey carried out in Namaqualand over an unnamed volcano-sedimentary massive sulphide prospect. The sulphide zone subcrops on the side of a low hill (Fig. 35). The climate is hot and very dry with occasional coastal fog (BWkn). Soils are thin (< 20 cm) with a poorly developed cambic B-horizon overlying the C-zone (Fig. 33). The A.horizon is only developed below individual specimens of the sparse xerophytic cover. Surficial Mn-staining is common. Fresh sulphide (pyrite) is exposed at surface in the more erosion-resistant quartzite units. Downslope, grey, gritty loamy soil (≤ 1m thick) showing poor profile development characterises areas underlain by biotite gneiss (Fig. 35).



Figure 35. Copper, lead and zinc content of residual soil in relation to unnamed massive sulphide prospect, Namaqualand. (Profile A-A', Fig. 60).

Soil samples were taken at 15cm depth or in the C-zone where soil is thin. The minus 80-mesh fraction was assayed (amongst others) for Cu, Pb and Zn by atomic absorption after a hot acid leach. Soil metal distribution indicated a bedrock source with a Pb : Zn : Cu ratio of about 7 : 4 : 1. Percussion drilling however, established a Pb : Zn : Cu ratio of 20 : 100 : 1, with lead occurring as finegrained galena, zinc and sugar-grained sphalerite and gahnite (zinc spinel), and very minor chalcopyrite. Soil pH was not determined but the abundant Mn-oxide staining and localised development of nodular pedogenic calcrete indicates a neutral to alkaline environment. It is suggested that oxidising nearsurface pyrite associated with the tuffaceous unit, keeps the pH sufficiently low to mobilise Zn^{2+} (pH of hydrolysis = 7.0), while Cu²⁺ and Pb²⁺ remain insoluble and are mechanically dispersed. The remaining zinc anomaly is attributed to clastic dispersion of gahnite (ZnAl204). For all elements assayed, peak soil anomalies coincide with peak bedrock metal content (verified by trench sampling). Secondary dispersion halos of Cu and Pb are close to background some 300 m downslope (10° - 13°) where a dry riverbed truncates the dispersion

trains. Zinc however, is still highly anomalous at the stream. Similar dispersion characteristics were noted by Wheatley (1978) over the Aggeneys and Gamsberg deposits, where soil copper and lead is restricted to the ore subcrop while zinc shows a 500m downslope dispersion. Lead and copper behave essentially as clastic grains in this environment while zinc shows some hydromorphic character.

Residual or near-residual soils give good geochemical responses that clearly delineate mineralisation in areas of moderate relief. Dispersion trains decay to background within about 300m for mechanically dispersed elements (pH of hydrolysis ≤ 6.5) but may be significantly longer for such elements as Zn and Mn in neutral soils and for Mo, V and Se in more alkaline soils (Fig. 4). Soils are thus not well suited to rapid reconnaissance exploration of large hilly areas but are useful sample media in conjunction with careful geological mapping, in stream sediment anomaly follow-up programs.

In semi-arid terrains, where moisture is more abundant, distinct profiles may develop. Soils forming from tonalite on the Peninsula Range, S. California (Fig. 15) show profile differentiation with respect to topographic position (Fig. 36B). Soils have pale (ochric) A-horizons. B-horizon properties vary markedly downslope. The Vista soil (Fig. 36C) has a cambic B characterised by alteration without evidence of illuviaction, whereas the Fallbrook soil, further downslope, has an argillic B characterised by the accumulation of illuvial silicate clay. The Bonsall soil has a nitric B represented by appreciable amounts of exchangeable sodium. The C-horizons are tonalite grus. The B-zone variation is attributed to the increased amount and greater duration of soil moisture with slope position (Fig. 36A). Soils on the lower slopes receive more water than these upslope because of lateral water movement, either at the surface or within the soil (Birkeland, 1974). Soils in hilly terrain in arid environments are thus stony and show little profile formation. In semi-arid areas, the B-zone may take on distinctive physical as well as chemical characteristics. Orientation studies, examining

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metal distribution in the soil profile, increase in importance with decreasing aridity and slope.



Figure 36. Toposequence of soils formed from tonalite, Peninsula Range, Southern California, under a semi-arid climate (Köppen BSk). (A) estimated soil water for 1965 - 66; (B) topographic and vegetative relationships; (C) distribution of clay with depth. (From : Birkeland, 1974).

Widespread formation of the A_o -horizon (Fig. 33) is precluded in arid and semi-arid environments by the lack of general vegetative cover. Organic debris does accumulate at the base of desert plants growing in all but the most arid areas. In areas of thin soil cover, both phreatophytes and xerophytes may have their root systems in mineralised rock. Hence, A_o -horizon sampling is a method of enhancing anomaly contrast, provided the chosen plant takes up the metal. For comparable results a single species should be selected for A_o horizon sampling.

An exercise comparing copper content of mountain soil B and A_o -zones with that of oak and mesquite leaves was undertaken by Clarke (1953) over the Ray porphyry copper occurrence Ray is situated in the hilly dissected terrain of Arizona that separates the Plateau province on the northeast from the broad flat desert plain in the southwest (Fig. 15). Soil samples were collected at a depth of 10cm and screened to minus 60-mesh. The A_o sample consisted of humus and some of the subsoil (*op cit.*). Copper content of A_o soil samples was up to an order of magnitude higher than that of nearby soils without organic matter. Clarke reports that the copper contents of the A_o soil horizon is very similar to that of the (ashed) leaves from which it was derived. Direct comparison between the latter is not strictly valid as a different acid leach was used on the ashed leaves. The technique does appear to have application in areas of deep or transported overburden where dispersion trains are difficult to detect by analysis of surficial material.

An interesting example of *integrated exploration* in a semi-arid environment (Köppen BSsk), where geological assessment of combined geophysical and geochemical data led to the formulation of an exploration model, is provided by Köksoy (1978). The Keban Pb-Zn mine is located in moderate to rugged terrain in central east Turkey. Skarn mineralisation is associated with syenite dyke intrusions at a marblesericite schist contact, and is located some 100 - 300 m below surface (Fig. 37). The ore is capped by a graphitic schist horizon which gives rise to numerous false Turam and IP anomalies.



Figure 37. Geological cross-section of the main Keban deposit, showing location of geochemical and geophysical anomalies. (From : Köksoy, 1978).

The minus 80-mesh fraction of the C-zone was assayed for total Cu, Pb, and Zn and cxZn (dithizone). A strong coincident Cu-Pb-Zn anomlay is located some 300 - 400 m west of the deposit and has been interpreted from geological mapping, to represent a leakage anomaly marking the surface position of an eastward-inclined channelway associated with the syenite dyke (Fig. 38). The cxZn anomaly east of the dyke is not related to mineralisation but represents hydromorphic dispersion from the mine dumps.

S.P. anomalies (-50 to -150 mV) occur along the eastern edge of the dyke and have been interpreted as outlining the water table-mineralised channelway intersection (op cit.).

Both geochemical and SP anomalies were drilled without penetrating mineralisation.



Figure 38. Lead, zinc, copper and cxZn of C-zone soil horizon in relation to underlying geology. (From : Köksoy, 1978).

Köksoy proposes an exploration model using geological (structural), geophysical and geochemical data. The geometric relationship between ore, surface anomalies and water-table depth is shown in Fig. 39.

Pathfinder Elements in Soils

Trace elements associated with ore minerals are incorporated into soils and may be used as pathfinders in regional and follow up exploration, particularly when their halos are larger than ore metal dispersions.

Mercury is strongly partitioned into sulphide minerals.

In Pb-Zn-Ag deposits, mercury is incorporated into sphalerite and sulphosalt. Similarly, in copper deposits mercury occurs principally in sulphosalt and in accessory sphalerite, although appreciable amounts may be tied up in copper minerals and pyrite (Jonasson and Sangster, 1975). In precious metal deposits mercury may occur as amalgams with elemental gold or silver, or in silver sulphosalt. The element is commonly present in tetrahedrite (≤21 weight%, schwatzite) and sphalerite (≤ 1 weight%), Ryall (1979).



Figure 39. Conceptual model showing the relationships between geochemical leakage and geophysical S.P. anomalies with respect to a blind ore deposit. (Köksoy, 1978).

In high rainfall areas, mercury vapour released during weathering of sulphides may migrate away from source in groundwater as the stable aqueous phases Hg₂Cl₂ and Hg°. There may be no surface anomalies. In arid climates, where water tables are deep, the high vapour pressure of mercury permits mercury gas to migrate to the surface (Chaffee, 1975) where it may escape or be fixed in the soil.

Retention of Hg in soils is governed by pH, porosity, amount and type of clays and organic constituents, and the presence of iron and manganese oxides (Ryall, 1979). In solutions high in chloride, the solubility of mercury is greatly increased by the formation of the uncharged HgCl₂ complex, or anionic complexes such as $HgCl_4^{2-}$. Similarly, at high pH, mercuric sulphide becomes highly mobile if much SO_4^{2-} is present (Hem, 1970). Saline soils are thus poor
sampling media as mercury would tend to be leached away.

Warren *et al.*, (1966) studied mercury distribution in various soil profiles over several Pb-Zn-Ag orebodies in British Columbia (Köppen D climates) and concluded that mercury tended to be concentrated in the B and C soil horizons over or close to mineralisation and in the A horizon away from mineralisation.

The use of mercury as a geochemical tracer in mineral exploration in a sem-arid environment has been studied by Wu and Mahaffey (1979). The mercury content of soils, rocks and soil gases was compared in an orientation study which demonstrated soils to be the best sampling medium. Soil mercury geochemistry surveys were conducted over two massive sulphide deposits in west central Arizona (Old Dick and Binghampton, Fig. 15). The minus 80-mesh fraction of surface soil was assayed within hours of collection with a gold-film Hg detector.

At Old Dick, the 100 ppb Hg contour outlines a 900 x 600 m area enclosing gossan outcrops and subcropping ore. A ground traverse over ore located at 150 m below the surface showed a response equal to that obtained over gossan. At Binghampton a 500 m wide Hg halo with values of 200 - 1000 ppb over a backgrounds of 50 ppb Hg coincides with two sulphide zones (Fig. 40b). The study suggests that hypogene Hg halos associated with proximal massive sulphides and their footwall alteration zones are larger and more intense than those associated with sulphides deposited distal to the hydrothermal centre. The mercury halos are about 75 times wider than the causative massive sulphide.

Mercury geochemistry thus appears to be an attractive exploration method for sulphide mineralisation in arid or semi-arid environments. Because of the high volatility of many mercury compounds, care must be observed in sample collection, preparation, storage and analysis. This tends to restrict the use of mercury to those areas where major element geochemistry is unsuccessful.

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(B)

Figure 40. (a) Simplified geology and Hg in soils, Binghampton area. (b) Profiles of Hg in soils along traverses AA' and BB', Binghampton area (From : Wu and Mahaffey, 1979)

The partitioning of Hg into the A soil horizon reported by Warren *et al.*, (1966) was examined on 130 samples from the semi-arid southwestern USA. No correlation could be found between soil mercury and organic matter content (Wu and Mahaffey, 1979) and hence the B or C soil horizons are the better mercury accumulators in semi-arid environments.

The influence of *mesh size* on anomaly contrast and relation to mineralisation was studied by Wargo and Powers (1978) who compared mercury, gold, and arsenic content of soils developed over the Saddle gold prospect, Nevada (Fig. 15). Gold mineralisation occurs as fine disseminations (< 2 - 8 µm in diameter) in cherty and carbonaceous rocks. Overall gold grade is 2.7 ppm. Bedrock is covered with 0.3 - 1m of residual lithic soil. Soil samples were split into a minus 80-mesh (0.175mm) fraction and a coarse minus 2,5 cm to plus 1.168 mm fraction. The latter consisted of limestone, chert and silicified limestone fragments and approximates a C-zone sample. The coarse fraction was crushed to minus 80-mesh and both fractions analysed.

Results (Fig. 41) show that analysis of gold in the coarse fraction clearly outlines mineralisation. Absolute gold values in this fraction (1.08 ppm) were considerably higher than in the fine fraction (0.12 ppm Au). Arsenic too, yielded larger anomalies in the coarse fraction. No mercury anomaly (> 150 ppb) was found in the minus 80-mesh fraction. The peak mercury value in the coarse fraction was 320 ppb and there appears to be poor correlation between the Hg and Au or As anomalies (op cit.). The authors conclude that the coarse fraction provides a more coherent exploration target than would the fine-fraction samples. Since mineralisation is associated with silicification, the coarse fraction may thus tend to concentrate these weathering resistant particles accounting for the higher values in the plus 14-mesh fraction. The authors conclude that mercury does not appear to add significantly to the development of an exploration target in the Saddle prospect area.

Soil mercury analysis remains a valuable tool however, for localising leakage halos related to blind mineralisation in geologically favourable areas.

Gossan Geochemistry

Gossans are the weathered outcrop expression of sulphide mineralisation and are formed by a complex oxidation process leading to a pronounced enrichment in iron oxides. Typically, gossan consists of quartz, hydrated iron oxides such as goethite, and a highly variable content of minor and trace elements. The gossan cap is underlain by an oxide zone leached of ore metals, which ideally grades downwards into an oxidised, metal-enriched zone of secondary sulphides overlying the hypogene orebody (Fig. 42). A good description of the gossan forming process is



given by Blain and Andrew (1977).

4. 4

Figure 41. Distribution of anomalous Au, As and Hg in the -1 +14 fraction (upper) and the -80 mesh fraction (lower) in relation to the horizontal projection of the mineralised area. (From : Wargo and Powers, 1978).

In deeply dissected terrain, gossan profiles may be entirely stripped by erosion. In more moderate terrain, preserved gossan profiles are modified by complex geomorphological and hydrological processes associated with recent climatic changes. Gossans in arid terrains (Gamsberg, Otjihase, Aggeneys, Fig. 7) are frequently unrelated to contemporary water tables (Blain and Andrew, 1977). Gossans at Prieska and Areachap (Fig. 7), developed on an extensive peneplaned Post-African surface, are largely destroyed by thick Late-Tertiary calcrete development associated with the onset of aridity. The Otjihase and Matchless (Fig. 7) gossans, related to a Gondwana erosion surface, are friable while gossans at Gorob (Fig. 7) on a much younger Quaternary surface are highly silicified (Andrew, 1980).



Figure 42. Typical gossan profile formed over a copper sulphide vein (From : Levinson, 1974).

In arid and semi-arid terrains, gossan searching and characterisation is an important base-metal exploration procedure. Gossan recognition is hampered by the occurrence of laterites and other ferruginous weathering products. The problem is further compounded by the chemical and morphological convergence of gossans and ironstone types (Fig. 43) during the more humid paleo-weathering cycle, and the subsequent effects of aridity described above.

Gossans have been defined as those hydrous iron oxides which overly economic mineralisation while false gossans or ironstones are any iron oxides, whether from sulphide veins, laterite, or any other source, which do not represent economic mineralisation (Gulson and Mizon, 1979 ; Moeskops, 1977) . Perhaps a less ambiguous definition classes gossans as those iron caps overlying base metal sulphides, economic or sub-economic (Fig. 43). The initial appraisal of a new gossanous outcrop firstly involves classifying it as a genuine gossan or some insignificant superficial deposit, and secondly, if genuine, what its characteristics suggest about the nature of the underlying mineralisation.



Figure 43. Nomenclature of ironstones, gossans, and other iron-rich surface expressions. (After : Taylor, 1979).

Initial characterisation involves evaluation of the gossan in its stratigraphic context. The association of a gossan in a ferruginous exhalite with stratiform barite and aluminous metasediments is diagnostic of volcanosedimentary sulphide mineralisation. Where the genetic affiliation is obscured by calcrete or supergene silicification, gossan trace-element geochemistry is the most important versatile and dependable criterion for their recognition (Andrew, 1977).

As sulphide minerals are weathered, a variable component of the liberated ore metals is generally retained within the gossan. Many other ironstones not derived from base metals may also contain significant accumulations of trace elements. Precise characterisation of a gossan relies on both mobile element content and the residual trace constituents of primary minerals (cassiterite, rutile, chromite, ilmenite, magnetite) and immobile elements (Au, Pt, Pd, Ir, Ag, As, Se, Ba, etc.). The distribution of these elements between true and false gossans has been reviewed by Blain and Andrew (1977). Their data (p. 145 *op cit*.) show that gossan geochemistry is characteristically variable with wide overlapping ranges of metal contents between true and false gossans. Nevertheless, this data may be used to characterise gossans (Fig. 44).



Figure 44. Scattergram of total Pb vs cxBa (as barite) for various gossans and other ironstones, southern Africa : •, economic Cu-Zn, massive sulphide gossans (2 localities, n = 63); ▲, sub-economic Cu-Zn semi-massive sulphide gossans (2 localities, n = 42); +, pyrite gossans (2 localities, n = 29); ×, ferruginised rocks, magnetite derived jaspers (3 localities, n = 39.) (After : Andrew, 1977).

Gossans developed over southern African, economic Cu-Zn deposits may readily be discriminated from false gossans and to a lesser degree from sub-economic Cu-Zn occurrences (Andrew, 1977). Lead and barium, initially fixed as relatively immobile sulphates in the supergene environment, are residually enriched under arid conditions, in the orebody gossans. On the plot of hx Pb vs cxBa (Fig. 44), 97 percent of false gossans plot in segment 3. Only 1½ percent of economic, and 2½ percent of subeconomic Cu-Zn gossans fall within the false-gossan domain (segment 3, Fig. 44) and would be misclassified. Gossans plotting in segment 2 are priority follow up targets. Since about 10½ percent of economic gossans fall in the sub-economic sector, plots in segment 1 (Fig. 44) are second priority targets. In the area studied, gossans derived from Cu-poor pyritepyrrhotite mineralisation exhibit higher Mn, Cu and Zn and much lower Ba content than gossans derived from massive Cu-Zn sulphides. The latter also have large soil Mn and P halos, (Black Mountain, Aggeneys area, Fig. 7.).

Classification methods, like the one described above, depending on diagnostic geochemical signatures are generally only applicable within ore districts (Blain and Andrew, 1977; Levinson, 1980) and specific geomorphological settings (Butt and Nickel, 1981).

Gossan characterisation on mobile elements alone frequently leads to misclassification. However, the effects of scavenging in false gossans may be partly overcome by using metal ratios. High Cu/Fe or Zn/Mn ratios are more likely indicators of base metal mineralisation than high absolute values of Cu and Zn (Levinson, 1974). An example where mobile elements were used to characterise true Ni gossans from pyritic gossans presently forming in the arid (Köppen Bsh, Fig. 22) southwest of Saudi Arabia is documented by Blain (1978). The area is hilly with moderate relief. Gossans over massive nickeliferous sulphides hosted in tuffaceous andesites and agglomerates, and gossans capping conformable pyritic lenses within basaltic and andesitic rocks were sampled. Analysis shows that gossans overlying low-grade nickel mineralisation can be distinguished from those over massive pyrite by their high Ni content. Higher contents of Cu, Co, M and Zn may be ancillary discriminators. (Fig. 45).

The highly refractory nature of gossans under arid climates promotes their residual accumulation and dispersion (Blain and Andrew, 1977). Talus aprons of cemented gossan boulders are common on the steep slopes below the pyritic gossan (Wadi Wassat area) and form a discrete class of transported gossan (Fig. 43). This resistant nature accounts for the persistence of gossan fragments in areas of thick pedogenic calcrete development, such as at Prieska and Areachap. Gossan sampling in arid areas is thus not confined to outcrop or subcrop but embraces the collection of fragments on deflation surfaces, and in soil, calcrete, alluvium or stream sediment.

	Ni	Cu	Co	Mn	Zn
Nickel gossan :	zone, Hadba	h (15 sam	ples)	- 22	
Geometric mea	an				
x, ppm	220	55	55	250	45
Range, ppm	25-1400	20-150	20-120	50-600	10-150
Pyrite gossan z	one, Wassat	(15 samp	les)		
Geometric mea	an				
x, ppm	30	20	20	150	20
Range, ppm	10-90	5-50	10-30	50-260	5-35

Figure 45. Trace element content of Hadbah nickel gossan and Wassat pyrite gossan. Range estimated at the 10 and 90 percentiles. (From : Blain, 1978).

Certain secondary minerals are characteristic of the arid environment. Brochantite, a blackish-green basic sulphate of copper is common in copper sulphide gossans in arid and semi-arid environments. Atacamite, a bright to blackishgreen basic chloride of copper forms in the arid saline conditions of the coastal desert of Chile. Malachite is a green basic cupric carbonate usually staining calcretes overlying copper mineralisation. Black, sooty, pulverulent chalcocite typifies recent supergene alteration in porphyry coppers (Haib, Fig. 7), and may easily be mistaken for manganese oxides. Yellow plumbojarosite in a basic sulphate of lead and ferric iron common on lead-iron sulphide gossans (Palache $et \ al., 1944$).

Black Mountain is the most westerly of the Aggeneys stratabound volcano-sedimentary polymetallic massive sulphide orebodies and illustrates several of the above-mentioned characteristics. The entire mountain is stained black by manganese oxides in stark contrast to the pale-brown colour of the surrounding hills. Bedded barite and malachitebrochantite-stained garnet quartzite crop out on its slopes. Large (≤ 2 cm) partly oxidised galena cubes occur in clusters in the ferruginous jasperoidal gossan at the very top of the mountain, a vantage point surely visited by numerous geologists, and yet, the potential of this zone remained unrecognised for more than 40 years after copper mineralisation was first reported !

Gossan geochemistry is characteristically variable, necessitating a large database to effect confident classification. Blain and Andrew (1977) suggest that computerassisted multivariate discriminant analysis is probably the best way of classifying ironstones and gossans within the exploration context. A more straightforward method for the geologist in the field, needing only a pocket calculator and some graph paper, is described by Smith *et al.*, (1979).

The authors use a simple display diagram (Fig. 46) to compare and contrast trace element content of false and true gossans. The multi-element character of a known false gossan population, preferably containing scavenged metal, is determined and plotted on a display diagram (Fig. 46A). The method involves :

- (i) Construction of cumulative frequency plots for each element in the reference ironstone population and calculation of the normal upper limits (thresholds), taken at the 95 percentile level. This level is assumed to mark the typical upper limit of the values in the false gossan and is used to define a discrimination level above which values are of interest to base metal exploration.
- (ii) Construction of display diagram (Fig. 46A) by plotting the range of an element (in the gossan being tested) parallel to the horizontal axis along the 95th percentile level calculated for that element in the reference population. Discrimination levels for 9 elements are shown in Fig. 46A.

A completed plot comparing an exploration gossan population with the reference population is shown in Fig. 46B. The Golden Grove gossan Sn, Bi and Ag means show relative



Figure 46A. Plot of Cu values in gossans plotted as a horizontal bar along the 95th percentile level of copper in the barren reference population.



Figure 46B. Display diagram comparing the character of the total Golden Grove gossan population with the 95th percentiles of the reference false gossan poplulation. High relative abundance of an element is shown by the displacement of the means to the right of the x1 or equal abundance diagonal. Maximum abundance factors for Cu, Bi, Sn and Ag are 20, 660, 4000 and 200 respectively, read against the dashed diagonal scale lines. The strong pathfinder character for the gossans is clear. (From : Smith et al., 1979).

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abundances in the range 10 - 80 times, while the Cu mean plots on the equal abundance (x1) line. In and Pb are depleted showing this to be a strongly leached base-metal gossan. The recommended sequence of gossan screening designed by Smith (1979) for the arid Bangemall Basin, Western Australia is shown in Fig. 47. The method, is applicable to any exploration program, especially in areas of deep leaching. Pathfinder elements will vary with the type of deposit sought.



Figure 47. Recommended flow chart for single-stage screening of Gossan-ironstone samples in Cu-Pb-Zn exploration (From : Smith, 1979).

Lead isotope ratio plots (Pb²⁰⁸/Pb²⁰⁴ and Pb²⁰⁷/Pb²⁰⁴ vs Pb²⁰⁶/Pb²⁰⁴) have been applied to stratiform massive sulphide gossans in Australia as a means of distinguishing false from true gossans (Gulson and Mizon, 1979). Primary Pb-Zn-Cu, Pb-Zn, and Zn-Pb sulphides and their gossans have similar, uniform isotope ratios when mineralisation exceeds 100,000 tons of Pb. Ratios are the same whether ores are hosted in volcanics, shales, or greenschists, and are unaffected by metamorphic grade or depth of gossan profile. False gossans, on the other hand, have distinctly more variable ratios. Pb isotopes are used in the drilling stage, to distinguish barren sulphides from those with economic potential, even though both may contain similar metal concentrations.

Numerous techniques are thus available to screen and classify gossans. These methods are particularly useful in arid regions where the genesis of gossan fragments dispersed in overburden is obscured.

Desert Varnish Geochemistry in Exploration

Desert varnish is a dark, lustrous to dull, manganeseand iron-rich coating up to 0.1 mm thick, which is widely distributed on exposed bedrock and on the surfaces of stones in talus, colluvium, and alluvial desert pavement accumulations in arid regions. At ground level, on embedded stones, an especially dark band of dense, shiny varnish, is developed. This zone is about 6 - 20 mm wide and is called the groundline band (Fig. 48). Associated with this dark coating is an orange veneer which develops in contact with the soil on the underside of embedded stones (Potter and Rossman, 1977). Engel and Sharp (1958) estimate that 75 percent of bedrock exposures of the southern Californian deserts have a recognizable degree of varnish. Desert varnish is probably the arid environment equivalent of the Fe and Mn staining found on stream sediments and float in humid areas. The latter have been widely used as sample media in regional geochemical surveys in wetter climates (Carpenter and Hayes, 1979). How representative is the trace metal content of desert varnish of the underlying rock, or its immediate surroundings ?

Desert varnish is found on all but the most friable rocks. Some of the most prominent patinas are developed on finer-grained basic lavas and metamorphic rocks. A weathered rind underlies the varnish. The distribution and origin of major and trace elements in varnish was studied by Engel and Sharp (1958). Analyses were done on varnish, the underlying weathered rind and fresh rock, as well as nearby soil and air-borne dust. Major elements (Fe, Mn, Ti and P) were determined by wet chemical methods and trace metals by spectrographic methods.



Figure 48. Sketches of bottom coat, ground-line band and desert varnish on a partly embedded stone. (From : Engel and Sharp, 1958).

The wet chemical data on 22 varnishes shows the most characteristic elements to be Mn and Fe. MnO has enrichment ratios with respect to the underlying rock, of 66 to 292. Iron is enriched 2 to 6 times. If the iron and manganese were derived from the underlying rock, the weathered rind and to a lesser extent the fresh rock should be depleted in these metals. Engel and Sharp (1958) found the opposite to be true (Fig. 49), and concluded that Fe and Mn have a source external to the rock on which it occurs.



Figure 49. Variations of selected elements in rock, rind and varnish on andesite from Sheephead, Mojave Desert (cf. Fig. 15), California. (From : Engel and Sharp, 1958).

The trace element content of all varnishes is similar in broad aspects regardless of location, lithology, or details of local environmental setting. The elements can be arranged into three groups on the basis of abundance (Fig. 50), and with minor exceptions, they tend to remain in these groups from sample to sample although their position in the group may change. In most specimens analysed, Ba, Co, Cr, Cu, Ni, Pb, Sr, Ti, V, and Y show a progressive increase from rock, through rind, to desert varnish (Fig. 49). Elements noted in the varnish but not in the underlying rock are Mo and The absence of a leaching gradient within the rock gives Sn. little support to the supposition that trace elements have come directly from the immediately underlying rock. This conclusion is supported by more recent researchers. (Hooke et al., 1969 and Potter and Rossman, 1979). Desert varnish is thus an unsuitable sample medium in detailed exploration geochemistry.

			Ppm	
			Mean	Range
Elements present in all var- nishes	Group I	Ti	3900	1000-9000
	>300	Ba	2200	500-4000
	ppm	Sr	700	100-2500
	1	Cu	260	30-900
		Ni	210	40-1500
	Group II	Zr	200	90-350
	50-300	Pb	180	90-300
	ppm	v	130	40-420
		Co	110	30-300
		La	110	40-200
		Y	80	50-200
		в	60	30-170
	Group	Cr	40	10-140
	111	Sc	20	10-50
	<50 ppm	Yb	6	3-15
		Cd	149	0-300
	W.	194	0-600	
Elements	Ag		0-80	
present in	Nb	14	0-70	
only some	Sn	44	0-30	
varnishes	Ga	- 2.2	0-15	
		Mo		0-10
		Bc		0-5
· · · · · · · · · · · · · · · · · · ·		Zn		0-200

Figure 50.

Average trace element content of 22 varnish samples from the Colorado and Mojave deserts of southern California. Analysis by spectrographic methods. (From : Engel and Sharp, 1958).

Potter and Rossman (1977) established that illitemontmorillonite clays comprise at least 70 percent of the black coat and 90 percent of the orange coat of varnishes. The presence of a variety of clays precludes direct synthesis from solution and the clay must thus be transported, probably as wind-borne dust, to the surface of the rock. The variability of trace element content in varnishes indicates a major proportion of dust to be derived locally from the surrounding mantle of weathered debris, as suggested by Engel and Sharp (1958). This dust may serve as a medium for capillary movement of varnishing solutions. Deposition of ferromanganese oxides within the clay matrix would cement the layer. The process is probably aided by the adsorption of Mn by illite. The scavenging ability of Mn may account for the high, erratic Cu and Ni content of some varnishes (Fig. 50).

No detailed study has as yet been made within a single district to establish positively whether or not desert varnish might be a useful geochemical sampling medium in exploration. The possibility of using desert varnish as a regional geochemical prospecting tool was assessed by Lakin *et al.*, (1963) on specimens collected in Death Valley (Fig. 15) and several localities in north eastern Nevada. Semiquantative spectrographic analyses were made on three samples from each site : (1) the varnish, (2) the rock chips or pebbles remaining after removal of the varnish with a dilute solution of ammonium oxalate and oxalic acid at pH 4, activated by UV, and (3) the surface 10 cm of grey porous desert soil in which the varnished pebbles were embedded.

Results show a striking correlation between Mn and Co content of varnish (r = 0.94). Cobalt content of varnish ranged from 2000 ppm in the sample with the highest Mn content (28%) to 30 ppm in that with the lowest (0.4%) Mn content. Pebbles and soil have uniformly low (5 - 20 ppm) cobalt content. A general correlation was noted between Mn and Ba, La, Mo, Ni, Pb, and Y. The sympathetic relationship between these elements and Mn suggests normal scavenging, and hence the content of these elements in desert varnish is not likely to be a meaningful indicator of mineralisation. Nevertheless, some correlation

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with ore provinces may be represented by the high B content (1000 ppm) of varnish from Death Valley, the high As (7000 ppm) and Sb (3000 ppm) content of that of the Edna Mountains, Nevada (Fig. 15), and the high Cu content (1500 ppm) of varnish from the Antler Peak - Copper Basin area, Nevada (Fig. 15). A similar correlation was found by Wheatley (1978) who noted high Zn (320 ppm) in desert varnish from the Aggeneys area, South Africa (Fig. 7).

In areas where desert varnish is abundantly developed, it may possibly be used as a sampling medium to detect regional geochemical trends. Successful application of varnish geochemistry in detailed exploration remains to be proven.

Terrain Mapping in Exploration

Terrain mapping, by means of airphoto interpretation (1:30 000 - 1:80 000 scale) backed up by ground checking, provides an excellent regional overview of ground conditions prior to entering an area. Carefully annotated terrain maps as described by Gartner (1981), can provide the geochemist with information that might otherwise not be available at the early planning stage of an exploration program. Terrain maps are used :

- (a) to separate areas of outcrop from areas of extensive overburden,
- (b) to discriminate between aeolian, water transported or in situ overburden,
- (c) to identify various erosion surfaces and determine the relative chronology of landform evolution,
- (d) to locate areas of hydrothermal alteration or vegetation anomalies and
- (e) to outline areas suitable for drainage sampling.

Terrain maps are particularly useful in regions of moderate relief which are characterised by a diversity of landform units. Maps are used by the geologist, geochemist and geophysicist in designing the optimum exploration approach for the prevailing ground conditions. Clark *et al.*, (1967) report on a preliminary terrain evaluation on the Copiapó district, southern Atacama Desert, northern Chile (Fig. 9). The study aimed at identifying geomorphological environments most favourable for the formation of extensive supergene alteration zones spatially related to porphyry copper deposits, and to delimit areas in the present landscape where these zones are most likely to have been preserved. Terrain maps were prepared from vertical aerial photographs on a scale of 1:60 000.

The study recognised the following stages of landform evolution :

- 1 : a major period of pediplanation consisting of three distinct periods of pediplain formation, separated by periods of dissection and canyon development. The most persistent zone of supergene massive chalcocite enrichment occurs at or very near the surface of the lowest pediplain,
- 2 : canyon cutting associated with marine regression,
- 3 : aggradation of valleys accompanying marine transgression,
- 4 : locally, intense weathering of alluvial deposits, and
- 5 : marine regression with dissection of aggradation deposits and modification of canyons cut in Stage 2.

On the basis of relations outlined above, the authors offer the following tentative exploration guides :

- (a) deposits exposed within canyons cut during Stage 5 are likely to have their high-grade enrichment zones eroded,
- (b) deposits eroded during Stage 2 canyon incision are unpromising although oxide enrichment zones may occur where the canyons are buried beneath younger alluvial deposits of Stage 3.
- (c) copper deposits underlying comparatively undissected remnants of the lowest pediplain of Stage 1 appear the most promising target for the search for enriched ore zones provided pedimentation has not truncated the entire supergene alteration profile to expose lowgrade hypogene ore.

Terrain maps can thus be used in regional exploration to eliminate areas unfavourable for ore preservation and in the follow-up stage, to assign priority ratings to geochemical anomalies.

An example where terrain maps would have limited unnecessary follow up of spurious soil anomalies is taken from a regional soil and stream sediment survey carried out in South West Africa during the early 1970's in order to locate strike extensions to known cupreous pyrite mineralisation. Pyrite-chalcopyrite ore, associated with magnetite quartzite crops out on the Cretaceous Gondwana erosion surface several kilometers northeast of Windhoek (Fig. 73). Soils are extensively leached, with an average Cu content of 10 ppm. Soils forming on the actively dissecting breakaway surface to the west, have an average Cu background value of 30 ppm Several anomalies, related to topographic (Fig. 51). features (Fig. 51, A - C) were drilled before their significance was appreciated. The problem was compounded by long dispersion trains of copper in stream sediments from some drainages in the breakaway area. These did reflect mineralisation, and were caused by mechanical dispersion of magnetite grains (with enclosed chalcopyrite blebs) associated with the mineralisation. The need for terrain evaluation at all stages of surface exploration, whether in arid or humid climates, cannot be overemphasised.



Figure 51. Hypothetical profile showing low (± 10 ppm) Cu values in soil on leached Gondwana Surface and higher background (± 30 ppm) on younger erosion surface. Responses A, B & C are false anomalies.

Trace Element Content of Magnetite in Exploration

Magnetite is fairly refractory during weathering and numerous grains survive the gossan forming process. Residual cores of magnetite in hematite pseudomorphs are common in the gossans of the Matchless Belt (South West Africa) and at Aggeneys (Andrew, 1980). Magnetite ($Fe^2 + Fe_2^3 + O_4$) may contain small amounts of trace elements diagnostic of the associated base-metal mineralisation. Fe^{2+} in magnetite may be replaced by Mg, Mn, Zn, Ni and Ti, while Fe^{3+} is partly replaced by Al, Ti, V and Cr (Ramdohr, 1969).

Levinson (1974) notes that high abundances of Ti and Zn in magnetite correlates with major Pb-Zn mineralisation, but low abundances of Ti and Zn correlate with major copper mineralisation. Alluvial magnetites derived from the stratiform Zn-Pb orebody at Gamsberg (Fig. 7) contain high total extractable Zn (2400 - 4400 ppm) for samples collected up to 8 km from the orebody (McLaurin, 1978). The magnetic fraction shows excellent enhancement and definition of anomalies. Dispersion trains are anomalous for up to 14 km from the deposit, and are in some cases longer than those defined by the minus 80-mesh silty material (Fig. 52). In a study on detrital magnetites derived from porphyry copper mineralisation in Ecuador, de Grys (1970) detected high concentrations of Cu and Zn in alluvial magnetites. Huff (1971) notes however, that the copper content is high in magnetites derived from both the porphyry stock and associated volcanics and may thus be used in regional rather than detailed porphyry exploration (see Fig. 59b).

Trace elements thus substitute for Fe^{2+} or Fe^{3+} in the magnetite lattice during crystallisation and attain characteristic anomalous concentrations in magnetites associated with volcanosedimentary and volcanogenic ores. Magnetite analysis is hampered by the high proportions of elemental iron (up to 70%), where the ratio of iron to trace constituent at the 0.001 percent level (10 ppm) is 70 000. The determination of trace constituents in such materials is difficult. Fortunately for prospecting purposes, analysis interferences are normally within tolerable limits. Since the trace metal content of magnetite may be used to define metallogenic provinces as well as specific exploration targets, governmental agencies may apply multi-element analysis of magnetites to identify areas most promising for exploration by private companies. To enhance the value of the resulting data set, an analytical procedure for the determination of as little as 1 - 2 ppm Ag, Bi, Cd, Co, Cu, Ni, Pb and Co in magnetite, is recommended (Nakagwa, 1975).





EXPLORATION IN AREAS OF SUBDUED RELIEF

In shield and platform deserts, landforms comprising the piedmont plain (Fig. 17) display subdued relief. In late maturity the old age (Fig. 31) the pediplain is the dominant topographic unit with occasional remnant inselbergs forming the only relief (Fig. 53b). Landforms associated with the inselberg landscape are shown in Fig. 54 and are characteristic of the western and eastern Sahara, Saudi Arabia, Bushmanland etc. Mountain and basin desert topography is produced by alternating horst and graben structure or tilted fault-block mountains. The intermontane basins or bolsons form the lowland areas between the fault-block mountain ranges (Fig. 55).



(a)

(B)

Figure 53. Landscape development in arid and semi-arid areas by lateral retreat showing the two major types of subdued relief; (a) a paleo-erosion surface or peneplain, and (b) the pediplain characteristic of the 'old age' stage of the erosion cycle. (From : Pritchard, 1979)

Flat areas in the shield deserts, mantled by transported overburden may extend for many kilometres and are a challenge to exploration geochemistry. Although intermontane basins are separated by areas of good exposure, the great thicknesses of graben infill make this an inhospitable environment for geochemical exploration. Generally, the successful application of geochemical methods becomes progressively more difficult with decrease in relief and consequent increase in thickness and diversity of overburden. Pediments are areas of degradation, frequently mantled by a thin cover of residual overburden, outcrop is common. Other landforms in regions of low relief are areas of aggradation, and hence most published case studies on geochemical exploration is subdued terrain focus on the pediment.

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Figure 54. Landforms associated with the inselberg landscape ; (a) exposed pediment surface, (b) piedmont surface with alluvial cover, (cf. Fig. 17). (From : Kesel, 1977).



Figure 55. Generalised cross-section of an intermontane basin or bolson typical of the Basin and Range Province, western United States. M = mountains, P = pediment, B = bajada or alluvial plain, Pl = playa. Vertical scale greatly exaggerated. (From : Reeves, 1980).

Alluvial Fans

Due to the sharp break in slope at the mountain front (Figs 13 and 54a), sediment-laden streams quickly deposit most of their load to form fan-shaped deposits of boulders, gravel, sand and minor amounts of silt and clay (Fig. 56). Fan deposits are crudely stratified and poorly sorted, and are common in the mountain and basin deserts of the southwestern United States, northern Chile, eastern Sahara, Pakistan and Iran (Cooke and Warren, 1973). Fans are also found in shield deserts where highlands border lowlands. Surface morphology of fans is composed of three basic elements :

- (1) fan channels giving rise to linear clastic dispersion patterns,
- (2) abandoned areas of former fan surfaces, and
- (3) depositional surfaces downslope of channels.



Figure 56. Idealised cross-section of an alluvial fan showing mudflow layers (aquicludes) interbedded with sandy gravel (aquifers). (From : Strahler, 1975).

Geochemical exploration in the alluvial fan environment either aims at detecting anomalous dispersion trains in the active channels of the fan that may be related to mineralisation in the uplands, or, at detecting mineralisation subcropping below the fan. No reported success for the latter situation could be found in the literature. The interbedded impervious mudflow layers within the sedimentary package tend to inhibit extensive vertical movement of groundwater and hence anomalous geochemical trends in surface materials do not reflect underlying bedrock mineralisation (Fig. 56). Ideally, fan head channel sediments may be sampled during regional geochemical surveys to detect the mineral potential of the adjacent rugged terrain.

Alluvial fan sediment as a sampling media in regional reconnaissance in the Sinai Peninsula is reported by Ayalon (1976). The area is arid (fig. 22) and comprises a narrow strip of flattish coastal plain in the north, and rugged desert topography in the south. The mountain ridge paralleling the coast is breached by 3 wadis (Fig. 57a). Wide alluvial fans mark their entry onto the coastal plain.



Figure 57. (a)

Sample localities along west coast of Gulf of Elat.

 (b) Distribution of heavy minerals in alluvial fan and wadi-opening stream-channel sediments along the western coast of the Gulf of Elat.
(From Auctor 1926)

(From : Ayalon, 1976).

Two hundred stream sediment samples were collected in drainage channels on alluvial fan heads and where the wadis exit from the mountain front. Heavy mineral concentrates were prepared from the minus 1 to plus 0.062 mm fraction and magnetite removed with a magnet. Magnetic fractions were prepared from the crushed concentrate with a Frantz separator and transparent minerals examined with a polarising microscope. Four well-defined heavy mineral provinces were identified (Fig. 57b) and reflect differences in nearby source rocks. Group I is derived from schists, gneisses and amphibolites. Group II from sandstones and Group III from acid-intermediate magmatic rocks. Group IV has a mixed sandstone-granite provenance. The study shows that the effects of dilution caused by poor sorting may be overcome by preparing heavy mineral concentrates.

Ayalon et al., (1981) analysed 128 selected samples from the above study by XRF, and seven magnetic fractions separated from 20 of these samples by DC emission spectrography. Results were evaluated by factor analysis and identify mineral-element associations typical of sandstone, granitic and metamorphic provenance. Plots of the groups and subgroups more clearly define the four groups outlined by Ayalon (1976) using only translucent minerals. The tabulated data (Ayalon et al., 1981) show highest mean values for Pb, Cu, and Ba in the 0.1 - 0.2 amp fraction associated with moderately anomalous iron oxide and Mn. Other heavy minerals are not anomalous in this fraction and the anomalous concentrations of Pb and Cu may be related to the presence of discrete sulphide grains in the concentrate. Barium reflects the presence of barite since during the heavy mineral concentrating process, most feldspars and other host minerals for barium were removed, Iron oxide and Mn are anomalous in the 0.1 amp fraction.

Both studies show alluvial fan environments to be amenable to regional geochemical prospecting provided the diffuse clastic dispersion halos are upgraded by heavy mineral concentrating and/or magnetic separation techniques before analysis.

If sampling of the alluvial fan environment is contemplated, it is recommended that sediments and concentrates be collected in the canyon or wadi mouth just before the channel enters the fan apex. Here it is much easier to determine the most recently deposited sediment, and dilution by debris flow and wind-blown sand, common on the fan, is largely avoided.

Pediment Environments

A pediment is a piedmont plain cut into bedrock and separated from the hillslope by an abrupt change of gradient. Pediments form broad, flat or gently sloping rock-floored or partly debris-mantled surfaces (Fig. 54) and occur between mountains where erosion is dominant, and the alluvial plain where deposition is preponderant (Cooke and Warren, 1973). The upper slope margin of pediments is clearly demarcated as the boundary between mountain and plain. The lower limit is defined as the line at which alluvial cover becomes continuous (Figs. 54a, 55).

The uplands exercise a dominating influence through contribution of runoff and supply of detritus, but erosional or depositional environments may prevail (Mabbutt, 1977). Pediments with a high percentage of exposure are rare. Thev generally comprise a complex surface with scattered outcrops surrounded by transported or residual overburden and are furrowed with a network of drainage channels. Pediment channels on the upper part of the piedmont plain form a distributary network of shallow rills which continue for about 100 m down the pediment depending on the extent of the alluvial apron (Fig. 54a, b). Rills give way to small gullies incised a few tens of centimetres into the mantle or bedrock. Where the autochthonous stream sediment or soil are suitable sample media in geochemical exploration. In areas of transported overburden, groundwater sampling and biogeochemistry are common exploration techniques.

Drainage Geochemistry

The main drainage features on pediments are upland stream channels, entering the pediment at re-entrants in the piedmont-mountain front junction, crossing the pediment, and ending in a playa lake in a closed drainage system. Stream channels of all orders on the pediment are shallow and sandy (Mabbutt, 1977).

The behaviour of basemetal dispersion trains in stream

sediments from the mountain front across an alluvial fan and a narrow pediment and onto the alluvial plain is described by Beeson *et al.*,(1975). The minus 200- and minus 80-mesh fractions of drainage alluvium collected across the Aggeneys massive sulphide ore zone were assayed by atomic absorption after a nitric-hydrochloric acid attack. Below the ore zone, the stream emerges onto the colluvium-mantled pediment across which Cu, Pb and Zn contents of the finer fraction drop rapidly $(1\frac{1}{2} - 2 \text{ km})$ to background levels for the alluvial plain (Fig. 58). The high background values across the sandy alluvial plain are maintained by influx of sediment at the 5.5 km downstream-point (Fig. 58), from a tributary draining the same mineralisation.

Zinc content of the minus 80-mesh fraction is 10 - 25 percent lower than that of the finer fraction. This difference is less marked in the case of copper and lead, suggesting these to be dispersed largely as clastic grains, while some of the zinc is hydromorphically transported. The slightly better anomaly contrast in the minus 200-mesh fraction does not justify the added time spent in looking for scarce silt or screening fines from the gravel fraction. This is borne out by data presented by McLaurin (1978) who sampled the Gamsberg deposit. McLaurin points out however that dispersion trains of coarser fractions (minus 10 to plus 40-mesh) are shorter than those of the minus 80-mesh fraction and give lower absolute values.

Similar conclusions were reached by Huff (1971), who carried out an orientation survey in several desert pediment washes draining basins with and without exposed porphyry copper mineralisation in the Lone Star district, Arizona (Fig. 15). The exercise concentrated on determining the subsample type that best distinguished washes draining mineralised from those draining non-mineralised areas, rather than on which subsample yielded the longest dispersion trains. Huff found that the minus 80-mesh fraction of backwater alluvium (stream bank, channel edge, silt behind boulders etc.) and that seived from the coarser gravels in the active channel yielded comparable results and both discriminated equally well between washes with exposed mineralisation



Figure 58. Distribution of lead, zinc, and copper in drainage sediments from the Aggeneys ore zone (solid line = -200 mesh and dotted line = -80 mesh). Analysis by atomic absorption after nitric-hydrochloric attack. (From : Beeson et al., 1975)

in their catchments and those with no mineralisation. The coarser minus 30- to plus 80-mesh fraction gave lower absolute values and poor ability to differentiate between anomalous and non-anomalous drainages (Fig. 59a). In areas where dilution by aeolian sand is not expected, the minus 80-mesh fraction of stream sediments appears to yield the best results.



(a)

(b)

Figure 59. (a) Histograms comparing Cu distribution of several subsample types in anomalous washes (black) with those in non-anomalous washes (crosshatched). (a) Analysis by atomic absorption after a hot acid leach, (b) analysis by spectrographic methods. Note different scales used in (a) and (b). (From : Huff, 1971).

Copper content of magnetic heavy minerals (collected with a hand magnet) failed to identify the washes draining copper deposits while that of the nonmagnetic heavy mineral concentrate gave good distinction ability (Fig. 59b). Huff also experimented with ultrasonic extracts of copper loosely held on grain surfaces. In this exercise the plus 80-mesh fraction of coarse sediment from the stream bed was placed in a beaker with metal-free water and treated for 1 hour in an ultrasonic cleaner to remove any loosely bonded material. The mixture was dried in an oven and the minus 80-mesh extracted to remove the concentrate. The treatment resulted in a marked concentration of copper and gave good distinction ability between anomalous and nonanomalous washes (Fig. 59b). The ultrasonic technique is similar to the cold extraction techniques which measure the hydromorphic component of samples. In this exercise however, the Cu tenor is expressed as a proportion of the residue and not of the whole sample and hence cold extractable Cu values appear higher than total extractable metal. Huff does not report on the percentage Cu removal by the ultrasonic process, but we can conclude that some of the copper is hydromorphically dispersed. The effectiveness of the method diminishes as the hydromorphic component of the dispersion decreases.

Although mineralised pebbles, nonmagnetic heavy minerals, and ultrasonic concentrates discriminate clearly between anomalous and non-anomalous drainage channels, it is suggested that these more time-consuming and hence expensive techniques only to be applied if orientation work suggests that silt-sized fractions do not yield the desired anomaly to background contrast. It should be remembered that optimum mesh fraction in sediment sampling is a function of climate and geologic and terrain conditions (Chaffee, 1975) and hence may change from place to place.

A drainage orientation study determining the behaviour of Cu, Pb, and Zn in various sediment fractions was carried out by the author during 1981. Zinc, lead, and minor copper mineralisation crops out on a hillside (Fig. 35.) forming the breakaway area between the African Surface and the younger Post-African Surface of the coastal plain (Fig. 73). The drainage channel is shallow and sandy and may be traced for 2 kms down the breakaway surface and for a further $1\frac{1}{2}$ kms onto the coastal plain where it fans out into a broad grass-covered clay pan (Fig. 60).

Stream sediment consists mainly of red, iron-oxide stained quartz grains and minor lithic fragments. Magnetic veneers are common at the surface and interbedded with the sediment. Backwater silt and clay occurs as thin crusts on

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the downstream side of low xerophytes and occasionally draping low sandbars present along the inner arc of bends in the river. Three main sample types were collected :

- (a) backwater silt and some of the underlying coarse fraction
- (b) sand from 15 20 cm depth in the centre of the stream
- (c) magnetite from blacksand veneers, collected with a hand magnet.



Figure 60. Sketch showing stream sample positions in relation to unnamed Zn-Pb±Cu sulphide ore body. Note that ore zone is truncated by the shear zone. Profile A-A' shown on Figure 35.

The magnetite fraction was milled and assayed by atomic absorption after a hot HCl - HNO₃ - HClO₄ - HF leach. Silt and gravel were split into three subfractions each (below) and analysed for partial extractable metal by atomic absorption after a cold 0.5M HCl leach, and for total metal content by multi-element X-ray fluorescence at the Anglo American Research Laboratories. The six subsamples investigated at each site are :

- 1. -40 to +80-mesh fraction of silt
- 2. -80 to +200-mesh fraction of silt
- 3. -200-mesh fraction of silt
- 4. -20 to +40-mesh fraction of gravel
- 5. -40 to +80-mesh fraction of gravel
- 6. -80 to +200-mesh fraction of gravel

Copper values in silt and gravels for both extractions do not exceed 35 ppm and show a maximum enrichment ratio with respect to background of 15 times (total analysis). Of the ore metals lead and zinc, the latter is the superior discriminator and is discussed below.

Total zinc (XRF) plots show that in terms of absolute metal content, the subfractions (1 - 6, above) may be arranged in the following order of decreasing metal content : $6 > 5 \cong 2 > 3 > 4 > 1$. The sequence for cxZn is : $3 > 6 \approx 2 > 1 > 5 > 4$. The minus 80 to plus 200-mesh fraction of gravel thus consistently yields highest Zn values (Fig. 61) in surveys utilising total metal content as an exploration criterion. The relationship holds for Zn as well as Pb and The minus 200-mesh fraction of silt yields highest metal Cu. content (In and Pb) where partial analyses are employed (Fig. 62). Partial analyses yields low contrast anomalies however, compared with total analyses (Fig. 61 and 62). On the coastal plain, 1 km downstream from the mineralised area (sample 17), the anomaly to background ratios for total Zn in subfractions 6, 5, and 4 are 13, 9, and 4 times respectively. Clearly the minus 80 to plus 200-mesh (or minus 80-mesh) of stream gravel is the best discriminator in terms of contrast and absolute metal value. Note that in the clay pan, where the gravel fraction is absent, the minus 200-mesh fraction (clay) yields highly anomalous cxZn values (Fig. 62). These results are in accord with those from the Haib exercise situated in more rugged terrain and a drier climate (p. 51). Both orientation exercises suggest that in terms of anomaly detection, the silty fraction of stream bar gravels yields comparable to much better results than coarser gravel or backwater silt samples. The problem of the scarcity of silt has been mentioned. These results agree with those of Chaffee et al., (p. 43), Filipek and Theobald (p. 44), Huff (p. 97) and Bugrov (p. 43).

The hot acid extractable Cu and Pb in magnetite are 1.3 times their respective local backgrounds. Similarly, Zn content of magnetite derived from the anomalous lithologies is twice local background value. The dispersion trains remained at anomalous concentrations over the length of the drainage. These low enrichment factors, as compared with the Gamsberg study (p.88), probably reflect variations in the intensity of the respective primary metallising events rather than in the secondary environment. Analysis of hot acidsoluble trace elements in magnetite is still a recommended technique for detecting volcanogenic and volcanosedimentary mineralisation.



Figure 61. Distribution of zinc in the -80 to +200-mesh fraction (solid line), and in the -40 to +80-mesh fraction (dashed line) of stream gravel. Analysis by X-ray fluorescence.



Figure 62. Distribution of cxZn in the -200-mesh fraction of backwater silt (solid line), and in the -80 to +200-mesh fraction of stream gravel (dashed line).

Stream sediment geochemistry in major drainage channels on pediments is analogous to alluvial fan sediment sampling in mountain and basin deserts where pediments are not always developed (Fig. 56), and is a useful technique in arid and semi-arid regions for locating mineralisation in adjacent mountainous areas,

Residual Pediment Soils in Exploration

The mechanisms of pediment formation are still the subject of debate amongst geomorphologists. Two main processes are advanced :

- (a) Retreat of the backing hillsope and extension of the pediment area and,
- (b) Mantle-controlled planation where relict weathered layers, formed during moister paleoclimates are eroded, exposing former weathering fronts (Fig. 63, cf. Figs. 31 and 32).



Figure 63. Sketch showing alternative hypotheses of pediment formation. "A" portrays formation by backwearing of original scarp (arrows) leaving pediment at its foot. "B" stresses a period of downweathering (arrows) followed by erosion to form present irregular bedrock topography, boulder-clad original hills, and remnants of originally thicker grus. (From : Moss, 1980).

In the back-wearing hypothesis, overburden is a mixture of residual and more abundant transported material while in the downwearing situation the mantle is largely residual in character. Clarification on this issue is important to geochemical exploration. Moss (1980), studying the Usery Mountain-Pass granitic pediments in the Sonoran Desert, Arizona (Fig. 15), concluded that the thick (\sim 30 m) granite grus accumulations and the irregular bedrock topography cannot be ascribed to the (arid) processes of sheetflow and rill action. He concludes that the area has been subjected to periods of long weathering, producing the grus, followed by a stage of stripping revealing the present granite surface or paleo-weathering front. Moss does not conclude that most pediments have formed in this way. Pitting through overburden to bedrock and profile logging and sampling is a common exploration practice in the early stages of regional exploration, and is strongly recommended before detailed follow-up soil sampling commences.

The results of a regional geochemical survey utilising thin residual soils mantling gently sloping pediments in eastern Botswana are detailed by Gordon (1973). Soil samples were collected at 61 m intervals along widely spaced traverses, selected to cross major fold closures that are readily discernable on aerial photographs. As the target Cu-Ni mineralisation is hosted in layered ultramafic-mafic complexes, samples were analysed by colorimetric methods using diquinolyl for copper and furildioxime for nickel. The use of the cold extraction technique eliminates false Ni anomalies generated by the liberation of lattice-bound silicate Ni by hot acid leach extractions.

A single sample of 150 ppm cxCu (over a general background of 10-60 ppm cxCu) indicated the presence of the Selebi orebody (Fig. 7) which is entirely covered by 0.5 to 1 m of soil.

Follow-up work outlined the Selebi Cu-Ni body and located and delineated the gossan-capped Pikwe ore zone. At Selebi, contours of 300 ppm cxCu and coincident 250 ppm cxNi in soils define the subsurface outline of the ore zone. Values are significantly higher at Pikwe. The anomaly width at Selebi is 100 m for both Cu and Ni and 150 and 200 m wide for Ni and Cu respectively at Pikwe showing limited lateral dispersion. Gordon further reports that high cxNi (300 - 1500 ppm) with
low coincident cxCu is the characteristic geochemical signature of subcropping barren serpentinites in this environment, while coincident high cxCu and cxNi (both > 200 ppm) in the soil outlines all known mineralisation in the area.

The case history shows that the hydromorphic component of the secondary dispersion halo of Cu and Ni in residual soils in this semi-arid environment (Köppen BShw, Fig. 7) is significant and may be used to advantage in Cu-Ni exploration.

Exploration in Alluvium-covered Areas.

Geochemical prospecting in pediment areas covered with extensive transported overburden poses special problems to the geochemist. In a geochemical study of alluvium-covered copper deposits in Pima County, Arizona, Huff (1970) investigated the ability of the Cu and Mo content of modern alluvium, older alluvium, carbonate-cemented paleo-regolith, groundwater, and plants to locate buried porphyry Cu-Mo mineralisation.

Within the Pima district (Fig. 15) several small hills rise above the alluvium-covered pediment surface. To the east, the pediment gives way to the alluvial plain where the overburden is substantially thicker (Fig. 64). A generalised overburden profile, as exposed in the mine open pits, is depicted in Fig. 65. Metal dispersion studies in the Pima district are hampered by 45 - 60m of transported overburden, the highly cemented conglomerate overlying bedrock, the presence in alluvium of detrital ore mineral fragments derived from distant outcrops, and contamination from nearby waste dumps.

Copper and molybdenum dispersion trains in modern alluvium could all be traced upstream to sources of contamination related to the ongoing mining activities. Copper content of residual soils over subcropping mineralisation on a low hill, drops to background within 60m, showing very restricted dispersion in this hot, dry desert environment (Köppen, BWhs). Samples collected from the red clay and calcrete of the older Pleistocene soil returned non-anomalous copper contents. Copper content (hot acid extractable) at various depths within the unconsolidated older alluvium shows a regular increase from 5 ppm near the present surface to 250 ppm just above the cemented regolith (Fig. 64). The presence within the alluvium of pebbles containing copper oxysalts suggests that this copper is detrital and that it could not have been derived from the Pima orebody underneath (op cit).



Figure 64. (a) Schematic cross-section of geology near the Mission-Pima deposits, Arizona. (From : Rose et al., 1979).



Figure 65. Idealised overburden profile over the Mission-Pima deposits, Arizona. (Data from : Huff, 1970)

Copper values in the carbonate-cemented conglomerate range from 4000 ppm at the base to 250 ppm at the top of the unit. The accumulation has been ascribed to precipitation of Cu from slightly acid groundwaters moving down the paleowater table gradient, upon interaction with the alkaline carbonate-rich conglomerate (see also Fig. 10b). No anomalous Mo could be detected in the carbonate conglomerate supporting the concentrating mechanism by Huff, (see Fig. 13). The anomalous area is about $1\frac{1}{2}$ km wide and extends into the unmineralised area about $2\frac{1}{2}$ km downslope of the concealed deposits.

Analysis of mesquite leaf ash returned several randomly distributed copper anomalies that appear to be spacially unrelated to the ore deposits. Molybdenum content of mesquite ash defined an irregular dispersion train down gradient of the deposit. Molydenum uptake by mesquite is however not only a function of Mo tenor of groundwater but also of water table depth. Biochemical Mo anomalies therefore reflect areas where the water table is shallow, and indicate Mo enrichments in nearby bedrock.

Groundwater in the Pima district has a pH of 7.1 - 7.6. Copper is relatively immobile under these conditions (Fig. 5) while Mo is fairly mobile (Fig. 13). Huff detected very low copper values in the groundwater. Molybdenum values ranged from 50 - 250 ppb (over a regional background of 4 ppb) and outlined a well-defined dispersion halo that could be detected for up to 13 km downslope from the Pima mine.

Huff (1970) proposes that further Cu-Mo targets in this area can be defined by :

- (a) analysis of borehole water and phreatophytes to locate other drainage basins rich in Mo,
- (b) widely spaced drilling in these basins to obtain geological data and determine copper content of the alluvial cover.

Drill hole location may be optimised by utilising the correlation between increasing molybdenum and increasing conductivity as an orebody is approached (Trost and Trautwein, 1975). These authors suggest using the ratio of log [Mo/K] in conjunction with a plot of [Mo/K] vs, log [Mo] to indicate the proximity of a buried oxidising porphyry copper deposits.

Hydrogeochemistry

Groundwater sampling is often the only source of geochemical information in flat arid and semi-arid regions blanketed by a thick cover of unconsolidated transported overburden. Water samples collected from existing boreholes are available cheaply and may delineate large hydromorphic anomalies which can subsequently be examined by water and bedrock sampling of follow-up percussion drilling. There is however, a paucity of literature on the successful application of groundwater methods in arid environments.

Rattigan *et al.* (1977), studying the Cattle Grid massive sulphide body, located below about 40 m of overburden in the Stuart Shelf area, South Australia (Fig. 76), concluded that no regular pattern could be demonstrated for Cu, Zn and Pb in groundwaters near the orebody.

In arid areas groundwater is normally alkaline except near oxidising sulphides. In this environment, very few metals are mobile. Mobility is governed by variations of lithologies within the aquifer, Eh and p^{H} , trace metal solubility and total dissolved solids (TDS). The effect of pH of hydrolysis has been discussed and will not be elaborated on again. It is important to realise that as groundwater moves through an aquifer the metal content as well as the TDS content increases. The absolute value of an element in groundwater is thus partly a function of distance traveled, and a high value need not reflect an anomalous situation. The trace metal to TDS ratio however, remains fairly constant and should be routinely calculated in hydrogeochemical surveys Rose *et al.*, 1979).

Oxidation of metal sulphides releases not only metal ions but also large amounts of sulphate to the groundwater system. The sulphate ion is both stable and mobile in the supergene environment (Dall'Aglio and Tonani, 1973). The sulphate ion, unlike base-metal ions, is not usually adsorbed or precipitated in neutral to alkaline groundwater and its dispersion halo may extend over tens of kilometers. Sulphate content of groundwater may thus be used as an indicator of sulphide (not necessarily economic) mineralisation.

Sulphate in groundwater may originate from rainfall, bedded evaporitic sulphate or from the oxidation of sulphides and hydrothermal H_2S emanations. Dall'Aglio and Tonani (1973) discuss a graphical technique which discriminates sulphide-derived sulphate from that derived from rain water, marine sediments and normal leaching of rocks (Fig. 66). The method does not clearly separate hydrothermal sulphate from base metal sulphide. The authors suggest that significant deviations from SO₄ vs Cl and SO₄ vs Ca plots of regional data indicates an anomalous situation. The study was carried out on surface waters in Tuscany, Italy.



Figure 66. Sulphate versus calcium content of 949 stream water samples from Tuscany, Italy. (From : Dall'Aglio and Tonani, 1973).

In arid and semi-arid regions, several factors may modify the SO4/Cl or SO4/Na ratios. Evaporation of water

from soil and transpiration by plants concentrate the dissolved solids to a significant degree. The Cl content will go up and if the content of Ca and HCO₃ rises enough to precipitate calcite, the ratio of SO_4 :Ca is changed (Rose *et al.*, 1979). Similarly under extreme evaporation, calcium and sulphate are removed from groundwater by the near surface precipitation of gypsum (CaSO₄·2H₂O), thus altering the SO₄/Cl ratio. Clearly, more research is needed before this method may be confidently applied in arid environments.

The interested reader is referred to papers (not available to the author) by Krainov (1971) and Naumov *et al.*, (1972) which deal with trace-metal mobility and concentrations in groundwaters associated with mineral deposits in desert areas.

Alluvial Plain Environments

The alluvial plains of shield deserts, or bajadas of mountain and basin deserts, consist of a series of shallowdipping, coalescing alluvial fans and comprise stratified, poorly sorted gravels and detritus interbedded with torrent and mudflow deposits (Cooke and Warren, 1973 : Mabbutt, 1977). The mountain front may be separated from the alluvial plain by a pediment surface (Figs. 54a and 55), or a series of coalescing alluvial fans (Figs. 18, 54b and 56). Outcrop is generally absent and the overburden derived from adjacent uplands. Geochemical information on bedrock mineralisation may be obtained directly by drilling or indirectly by sampling groundwater, biological materials or soil vapours. Terrace gravels may be sampled in drainage basins with short piedmont plain lengths (Fig. 17b). The application of hydrogeochemistry and biogeochemistry as discussed in previous sections, applies equally to the alluvial plain or bajada environment.

Vapour Geochemistry

One of the remaining problems in mineral exploration

is the location of mineralisation concealed beneath barren exotic overburden. The problem is particularly severe in arid environments with deep water tables where readily detectable hydromorphic dispersion halos are absent in the near surface environment, and boreholes for groundwater sampling are widely scattered or absent. This porous, dry cover does however, promote the movement of highly mobile gases such as CO2, COS, He, H2S, Hg, I2, N2, O2, and SO2 generated by inorganic and bacterial oxidation of sulphides, the degassing of ore minerals, and the atomic disintegration of radioactive minerals (Boyle, 1982b). Soil vapour methods are thus applicable to locating dispersion patterns formed by highly mobile and relatively chemically inert gases released from ore minerals within the zone of weathering.

Sampling problems are a major constraint on the application of vapour techniques in exploration. Analysis of soil gas pumped from thin probes or drillholes is less susceptible to atmospheric dilution effects than sampling air near groundlevel. Nevertheless, the amount of gases trapped in soil interstices varies with barometric pressure, temperature, humidity and rainfall (Levinson, 1974), Rose *et al.*, 1979). Gas collection techniques are detailed by Dyck and Meilleur, (1972). Problems of loss during storage by diffusion or leakage may be avoided by using mobile analytical units such as those described by Lovell *et al.*, (1980) for CO₂ and Rn-Hg ; Friedman and Denton (1976) for He.

During the oxidation of sulphide, the oxygen consumed is derived from the interstitial air of the overburden (equation 1) and the sulphuric acid produced decomposes carbonate minerals within the gangue or country rock, generating carbon dioxide (equation 2) :

 $4FeS_{2} + 15O_{2} + 8H_{2}O \rightarrow 2Fe_{2}O_{3} + 8H_{2}SO_{4} \qquad \dots 1$ CaCO₃ + H₂SO₄ \rightarrow CaSO₄ + CO₂ + H₂O $\qquad \dots 2$ Anomalously high contents of CO₂ and low O₂ in overburden indicate active oxidising subsurface sulphide deposits, (Fig. 67). In the absence of carbonate, little CO₂ is produced, but a marked O₂ depletion is still detectable (Joyce, 1976). Studies by Lovell *et al.*,(1980) in Saudi Arabia, South West Africa and western United States showed background levels of CO₂ and O₂ in soil air of arid and semi-arid regions to be much lower than in temperate regions, creating some problems of analytical sensitivity and precision at background levels. Few misleading anomalies were generated however, (*op cit.*).



Figure 67. Carbon dioxide and oxygen contents of soil air at 1.5 m depth above a pyritised fault zone. (From : Rose et al., 1979).

Sulphur dioxide dissolves in water to form a weak acid (H_2SO_3) and its dissociation products (HSO_3^{-}, SO_3^{2-}) , which in turn are readily oxidised to sulphuric acid (H₂SO₄). Thus it seems unlikely that much SO, could escape from the site of oxidising sulphides except under arid conditions. Lovell et al., (1980) experimented with collecting sulphur gases on molecular sieves buried along traverse lines across mineralisation in the Atacama desert, northern Chile. The method was not found to be successful for a number of reasons : two visits to the field were required to emplace and recover the gas collectors ; the molecular sieve was found to be prone to contamination by sulphur gases in atmospheric air both before emplacement and after collection ; and as noted by Hinkle and Kantor (1978), best results are only achieved after a burial time of two months.

Since soils have the advantage of being in equilibrium with the soil air, the use of the soil itself as an absorbent for sulphur gases was tested at Johnsons Camp copperzinc deposit, Arizona (Fig. 15). The ore is hosted in limestone and subcrops beneath a gently sloping alluvial plain. The alluvium consists of gravels, conglomerates and calcrete, thickening from about 10 m over the southwestern ore zone to about 100 m over the larger north easterly ore zone (Fig. 68). Anomalous sulphur was recorded by Lovell et al., (1980) over both ore zones (Fig. 68). The same area was tested by Hinkel and Kantor (1978) who placed molecular sieves at 30 - 45 cm depths in the soil. Sieves were removed after 8 weeks and absorbed soil gases analysed by gas chromatography. No CS2 or SO2 was detected in any of the samples. Anomalies of COS, H2S, and CO2 were located above and peripheral to the deposits. The anomalous responses away from mineralisation look the same as those over mineralisation and may reflect lateral variations in permeability of the underlying alluvium. Analysis of gas adsorbed onto soil appears, in this case, to give better anomaly definition than that of soil pore gas. Similar conclusions were reached by Wu and Mahaffey (1979) and McNerney (1980) studying the dispersion of mercury in soils, soil gases and rocks.



Figure 68. Sulphur gases adsorbed onto soils at Johnson Camp copper-zinc deposit, Arizona. (From : Lovell et al., 1980).

Eremeev et al., (1973) detected anomalous concentrations of helium in the near-surface groundwaters (10 - 30 m below thesurface) circulating through a variety of faulted or structure-controlled sulphide deposits (Fig. 69). Although He tends to delineate deep permeable crustal fracture zones, Zhirov et al., (1975) report He and Ar as primary constituents of Cu-Ni sulphide ores in the Urals, Kazakhstan and Caucasus.



Figure 69. Helium halos in near-surface groundwaters circulating through faulted and structure-controlled ore bodies : (a) Barchensk carbonatite deposit, north Kazakhstan ; (b) Auriferous quartz vein deposit, Bestube, north Kazakhstan ; (c) Leadzinc-barite deposit, Bastoba, central Kazakhstan ; (d) Urup copper-pyrite deposit, Caucasus (From : Eremeev et al., 1973).

Soil vapour geochemistry, as a base metal exploration technique enjoys little credibility with many mining companies due to the large number of spurious anomalies generated by changes in gas concentrations resulting from daily meteorological variations, and from the distribution of lithological permeability barriers (to gases or groundwater) within the overburden. This, plus the complex sample collection, preparation and storage procedures, limits the usefulness of the technique. However, the method offers deep geochemical penetration in areas of thick transported overburden, particularly in arid environments, and awaits development.

Playa Environments

Playa is a general term for a variety of topographic depressions and dessicated or dune-covered former lakes that are common in arid and semi-arid regions of the world. Primary causes of playa basin formation vary in importance between geologic and climatic settings. Block-faulting is characteristic of mountain and basin deserts (south western United States) whereas the large tectonic lake basins in shield and platform deserts (Lake Chad) are commonly caused by broad shallow warping. Deflation basins occur in flat landscapes underlain by unconsolidated alluvium or lacustrine sediments. The pans of the semiarid Kalahari result from wind erosion of a surface loosened by animal activity (Mabbutt, 1977). Basins impounded by barriers of wind-blown sand and alluvium are charateristic of flat plains and valley floors near the terminal sectors of drainages or on the margins of dunefields, where aeolian sand has invaded river systems.

Some playas receive their total water budget from desert downpours or runoff from adjacent highlands and are characterised by smooth, hard, dry, clayey surfaces with little calcrete development and an absence of evaporite minerals. Trace-metal content of pan sediments may thus reflect mineralisation in the source terrain, as was noted by Beeson *et al.*, (1975) who located anomalous values of Cu and Zn in a pan, 12 km downstream from the Aggeneys massive sulphide deposit (Fig. 58). Similar results were obtained by Leach *et al.*,(1980) who recorded anomalous concentrations of zinc in the Roach Lake playa sediments, Nevada (Fig. 15) that are possibly related to the zinc deposits in the basin. Anomalous gold (\leq 8 ppb) and tungsten (10 - 20 ppm) in the same playa reflect gold prospects in the bordering Precambrian granites. Samples from nearby playas with no known mineralisation in their catchment areas, returned background values for these metals.

If surface runoff is insufficient to reach the playa, groundwater recharged in the alluvial fans, pediment surface, and mountain aquifers moves towards the low part of the basin where discharge may occur through springs near the playa edge, by capillary action from beneath the playa surface, or from plant evapotranspiration (Cooke and Warren, 1973). The high evaporation rate results in a steady accumulation of such salts as sodium chloride, sodium carbonate, sodium sulphate, borates and nitrates which are exploitable in their own right. The largest known single tungsten resource in the United States, calculated at 77 million kg of WO₃, is held in the interstitial brines of Searles Lake, California (Fig. 15) where concentrations as high as 70 ppm WO₃ are present in the lake brines (Carpenter and Garrett, 1959 in Leach *et al.*, 1980).

Interpretation of base-metal anomalies in playas with both surface and groundwater recharge is hampered by the need to distinguish between the surface clastic and groundwater hydromorphic dispersion components of the anomaly. Tracing the seepage anomaly to source is problematical. In the Basin and Range province the depth of basin fill may exceed 3 km (Reeves, 1980) and it is unlikely that bedrock mineralisation below the playa, will reflect in the surficial silts and clays.

The ability of surface playa sediments to reflect subcropping base-metal mineralisation was tested by Friederich and Christensen (1977) over the Lake Yindarlgooda black shalehosted massive sulphide deposit (Fig. 76), Eastern Goldfields greenstone belt, Western Australia. Local physiography is characterised by two distinct land surfaces : a Mesozoic-Tertiary peneplain, extensively laterised during the Pliocene, and a lower Quaternary surface represented by clay pans and playa lakes which evolved from the early Tertiary drainage system with the onset of aridity. Friederich and Christensen sampled solonchaks (Figs. 11 & 12D) developed in the playa environment from the older alluvium overlying mineralisation. The solonchak is thin $(\leq 2\frac{1}{2} m)$ and shows good profile development. The water table is shallow (∿ 1m). The soil profile and underlying bedrock were sampled by auger. Rocks were subjected to total analysis (25% HNO₃ followed by atomic absorption) while the minus 80-mesh fraction of soils was treated with a 1% EDTA leach in order to establish the adsorbed portion of the total metal content.

Results show that the trace element variation within bedrock lithologies is not reflected in the solonchak profile, which the authors attribute to the poor sorbtion capacity of kaolinite, comprising 80 percent of the solonchak clay mineral fraction. The lack of correlation between grain size and adsorbed Fe, Ni and Zn in the solonchak led Friederich and Christensen to conclude that the trace element distribution is not influenced by hydromorphic dispersion from the underlying mineralisation but by the original composition of the alluvium. The optimum exploration approach in this playa environment involves sampling weathered bedrock below the playa lake sediments, with an auger.

In a similar geomorphological setting, in the Stuart Shelf area, South Australia (Fig. 76), Rattigan *et al.*, (1977) sampled salt lake muds and underlying lithologies. Shalehosted copper mineralisation is located at a quartzite-sandstone interface. An unmineralised portion of this contact subcrops below the playa lake. Mud and bedrock samples were assayed by atomic absorption following a hot concentrated perchloric leach. Anomalous concentrations of Cu and Zn (up to 24 and 5 times background) in the lake bottom muds coincide with the favourable horizon. Lead values in the bottom muds are depleted. This indicates a measure of hydromorphic dispersion for Cu and Zn along the contact zone and precipitation within the mud near the contact. The survey also established that metal values are generally uniform through the mud profile with slightly lower values in the top 50 cm of mud. The authors agree with Friederich and Christensen (1977) that in this arid, saline terrain, where bedrock is masked by superficial strata, drilling to bedrock (by percussion or auger) is the most successful technique in locating primary and secondary dispersion halos.

Exploration in Areas of Aeolian Cover

Sand desert, the poplular image of an arid landscape, forms only a minor part of many deserts, for instance, less than 2 percent in North America. Sand covers about 15 percent of the arid Sahara but 50 percent of the semi-arid Australian deserts (Mabbutt, 1977). Desert sands consist largely of quartz grains and lesser amount of feldspar. The fine fraction commonly includes a small proportion of heavy minerals such as amphiboles, garnets, ilmenite and magnetite. The main source is alluvium, shown by the common occurrence of sand desert in lowlands beyond river terminals.

Very little information is published on clastic dispersion patterns in aeolian deposits. Bugrov (1974) reports the secondary concentration of weathering-resistant heavy minerals (e.g. Sn, W, Nb, Ta, Zr etc) on deflation surfaces within aeolian sediments, that yield anomalous results out of porportion to the metal content of the bedrock source. Rose *et al.*, (1979) mention an asymmetrical dispersion halo, distorted in the direction of the prevailing wind, in sands surrounding a mineralised hill in the Sahara.

The common approach to base metal exploration in areas of aeolian cover is to follow up air-borne geophysical anomalies by drilling. Metal dispersions have been detected by groundwater geochemistry (Huff, 1970), biogeochemistry (Cole and Le Roux, 1978) and vapour sniffing techniques (Lovell *et al.*, 1980). Less commonly applied techniques in regions of wind-blown sand are termite mound sampling and surface microlayer sampling.

Termite Mound Sampling

Termite mounds may have potential as sampling media, particularly in areas of exotic overburden where termites, in the course of excavating galleries to the water table, transport significant amounts of weathered and resistate In Botswana, termite mound sampling material to the surface. has been used successfully in the search for diamond pipes by identifying the kimberlitic minerals pyrope and chrome diopside, brought to the surface from beneath as much as 40 m of Kalahari sand (Levinson, 1980). Geochemical sampling of termite mounds thus appears to offer a method of prospecting for ores with resistate minerals such as cassiterite, zincian magnetite, scheelite and gold in the weathered zone. Watson (1972) has shown that termites tend to avoid carrying particles larger than 1.26 mm (their sieve size) and hence the absence of a particular refractory mineral in a termite mound need not reflect its absence in the underlying bedrock.

The distribution of gold in termite mounds and nearby soils developed on Kalahari sand overlying known gold mineralisation at Gold Anomaly (Fig. 7), was studied by Watson (1972). Gold occurs in fissures in basement at a depth of 23 m, some 4 m above water table. It is interesting to note that the termite mound is alkaline in reaction and rich in carbonates whereas the soil is acid. The minus 1.26 mm fraction was separated from 23 kg samples of termite mound collected from 0 - 60 cm depth and from three soil horizons and the underlying pebble bed, which ranged from 150 to 412 cm below the surface. A heavy mineral concentrate, prepared from the minus 1.26 mm fraction, was assayed by fire assay and gold gold content expressed as a proportion by weight of the minus 1.26 mm fraction. The proportion of this fraction ranges from a maximum of 58 percent in top soils to a minimum of 32 percent in the pebble bed.

Analysis of results (Fig. 70) show that the difference bet-

ween the mean concentration of gold in termite mounds and the maximum value in an adjacent soil profile is small (0.051 and 0.047 ppm Au respectively), and not statistically significant. This shows that gold in termite mounds could have been derived from the surrounding (aeolian) soils. The termite mound with the highest value (0.52 ppm Au) is situated on soil which contains low concentrations of gold (0.07 ppm Au) which shows the more plausible situation that topsoils are formed by erosion of termite mounds, containing gold from the underlying bedrock.



Figure 70. Distribution of gold at Gold Anomaly in (a) termite mounds and (b) soil profiles. Note : soil gold value above is taken from the horizon with the highest concentration of gold, and is not the mean value for the four horizons. (From : Watson, 1972).

Brooks (1982), citing West (1970), reports that experiments carried out in the Silobela area (Fig. 7), Zimbabwe, anomalous gold values in termitaria of *Macrotermens natalensis* in three localised areas, accurately delineated the payable section of three modern gold mines. At the Lion Mine, anthill sampling indicated a previously unknown orebody. A gold mine now in operation, named Termite Mine, was found by this method alone (Brooks, 1982).

From a study of copper distribution in a termitary located on copper-enriched soils at Baluba, central Zambia (Fig. 71), Tooms and Webb (1961) showed that most of the material was derived from the A-horizon. Brown (1971) reached a similar conclusion from a study of Kalahari sand-covered copper mineralisation in northwest Zambia. Copper content of termite mounds is anomalous over bedrock mineralisation, but values are significantly lower than in adjacent soil profiles clearly indicating that the distribution of copper in Kalahari sand is due mainly to hydromorphic agencies.



Figure 71. Distribution of copper in a termitary and underlying soil in the vicinity of mineralisation, Baluba. (From : Tooms and Webb, 1961).

Similar hydromorphic dispersion in Kalahari sand was noted by Watson (1970) who detected Zn anomalies in the C-horizon of soils developed over weakly mineralised mica schist (Fig. 72) at Turtle mine, Zimbabwe (Fig. 7). Termite mounds at the same locality were less anomalous than the C-horizon and contained no recognizable fragments of mica schist, indicating that the termites were not effective in dispersing coarse fragments from the deeper layers. Termite mounds contain more zinc than the top soil (0-60 cm) and Watson concludes that zinc in the termitaries could have been derived from the zinc-rich



subsoil at less than 3 metre depth.

Figure 72. Distribution of Cu, Pb and Zn in Kalahari soil profiles near Turtle mine. (Analysis by atomic absorption following 60% perchloric - 5% nitric, digestion). Climate : Köppen BShU (From : Watson, 1970).

The papers reviewed suggest that termites readily disperse chemically inert refractory minerals from recorded depths of up to 40 metres. Where termitaries are located over soils with significant hydromorphic base-metal dispersions, termites seem to be averse to bringing to surface soil with highly anomalous (and toxic?) base-metal concentrations. Nevertheless, it has been shown that termite mounds return slightly higher copper and zinc values than the topsoil (0-60cm) and should be considered as sampling media in sand-covered areas. Termitary sampling is especially recommended in areas of constantly shifting sand where surface grains may not be in geochemical equilibrium with the temporarily stabilised underlying sands. Samples should be assayed not only for the common base metals but also for the pathfinder elements. The strength of chemical attack that gives best anomaly to background contrast depends on the dispersion : total analysis for refractory grains, and a carefully selected partial extraction for hydrohydromorphically dispersed elements.

Surface Microlayer Sampling

Hydromorphic dispersion of base metals through barren aeolian overburden, under semi-arid conditions, has been demonstrated (Rose et al., 1979; Watson, 1970; Tooms and Webb, 1961). Similarly movement of ore-related gases and their fixing in the surface layer of transported soils has been shown to be a viable migration mechanism in semi-arid areas (Lovell et al., 1980 ; McNerney, 1980). It is not unreasonable therefore to suppose that under arid and very arid conditions where evaporaton far exceeds precipitation, groundwater migrates upwards carrying with it ionic material in solution. On evaporation, much of the ionic component will tend to be left coating grain surfaces. According to Bradshaw and Thomson (1979b) this coating, whether originating from hydromorphic or gaseous dispersion, can be anticipated to be strongest in the surface 1 - 2 mm, the surface microlayer, and decrease in concentration with depth (Fig. 11b).

The surface microlayer technique aims at uniquely identifying that portion of the element which is added to the soil, from any residual background component related to the chemistry of the overburden parent material. The minus 200-micron fraction can be highly contaminated with material that has undergone atmospheric dispersion from distant sources, and should be removed from the sample (Barringer and Bradshaw, 1979). The remaining fraction, excluding plant fragments, is suitable for analysis. Orientation work should establish which partial analytical procedure is blind to background metal content while efficiently removing the loosely bonded metal added from depth. To optimise contrast, samples should be collected on the lee side of wind barriers where the more stable soil has attained maximum chemical equilibrium with the groundwater/ vapour regime. Similarly, sampling is not recommended immediately after rain, when part of the microlayer may be leached downwards with the infiltrating rainwater (Fig. 11a). The time taken to re-establish chemical equilibrium at

surface is probably equal to that taken for the wetted soil layer to dry out.

No successful application of this technique in arid environments, to locate mineralisation below thick alluvium could be found in the literature. However, the method has great potential in areas of aeolian overburden where conventional geochemistry is unsuccessful.

GEOCHEMICAL EXPLORATION IN DURICRUST TERRAIN

Over large parts of southern Africa a succession of stable planation surfaces (peneplains) have developed from Late Paleozoic onward (Carlisle, 1980). Similarly, in Australia, parts of the landscape are the result of over 70 m.y. of subaerial exposure. During this time, these surfaces have been subjected to weathering under a variety of climatic conditions resulting in deep leaching and the formation of laterite, calcrete or minor silcrete.

In Australia, climates tended to be temperate or warm in the Mesozoic, becoming humid tropical or subtropical in the Oligocene-Miocene. In areas of tectonic stability, these climates gave rise to a deeply weathered laterite profile which has subsequently been partially eroded, resulting in extensive planation (Butt and Smith, 1980). Subsequent uplift, accompanied by erosion has locally caused partial or total stripping and dissection of the profile during the Quaternary. The relatively wet climate responsible for the lateritisation gave way to the current semi-arid conditions resulting in a lowering of the water table and the development of sand plains, endorheic drainage and salt playas on the Quaternary surface (Nickel and Thornber, 1977).

The smooth Gondwana surface represents the oldest planation surface in the arid and semi-arid western part of southern Africa (Fig. 73). The surface is deeply leached. The late Cretaceous - Middle Tertiary African Planation forms the most perfectly planed surface in Africa (Carlisle, 1980), and evolved roughly contemporaneous with the Australian episode of lateritisation. The surface records planation from temperate to more arid conditions evidenced by the extensive calcrete horizons developed in correlative sediments in the Kalahari (Carlisle, 1980). Rejuvenation resulted in Miocene and Pliocene valley-floor pediplanation. The main period of calcretisation is related to the semiarid climatic conditions prevailing during the Pliocene-Pleistocene. Calcretes are not forming under today's more arid regime (Carlisle, 1980). Pedogenic calcretes are being

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modified by the normal illuvial processes of the current arid regime.



Figure 73. Map showing geomorphic surfaces in the arid and semi-arid southern Africa. (From : Carlisle, 1980)

Deep weathering by lateritisation or calcretisation masks the original geochemical nature of mineralisation. The lateritisation process produces mineralogical and chemical changes in rocks and ores, often resulting in weathering products with a similar chemistry and appearance. Calcretisation tends to obliterate gossan caps by fragmentation until no clearly recognizable surface expression remains. The alkaline reaction of calcreted ground severely restricts metal dispersion. The objective of geochemical investigations in laterised or calcretised terrain is to determine those sampling and analytical procedures that yield high-contrast geochemical signatures in the surficial weathered material, diagnostic of the underlying source rocks. The geochemical character of the surficial environment reflects the cumulative imprint of all preceeding surface processes. Hence, the application of a diagnostic geochemical signature in the interpretative stage, should be restricted to data gathered from the specific planation surface for which it was determined.

Exploration in Calcrete-covered Areas

Calcretes are common in the western two thirds of the African sub-continent south of latitude 17°S. They comprise any material of almost any consistency and carbonate content, formed within the regolith by *in situ* cementation and/or precipitated from the soil water or groundwater (Netterberg, 1980). The reader is referred to the last-mentioned paper with its extensive reference list, for detailed information on calcrete genesis.

Of importance to the geochemist it the distinction between pedogenic (endogenic) calcrete and non-pedogenic (valley, exogenic) calcrete (Chaffee, 1975). The fundamental difference between the two types is that pedogenic calcretes result from predominantly vertical redistribution of Ca, Mg, CO_3^{2-} and trace elements within the soil moisture zone. They are extensive, thin horizons within the soil and are mainly illuvial (Figs 11a, 33b). Pedogenic calcretes from in semi-arid environments (Carlisle, 1980). Non-pedogenic calcretes result from lateral transport of solutions towards favourable sites of deposition and form under much more arid climate than pedogenic calcretes (Carlisle, 1980).

Typical pedogenic calcretes in Bushmanland are friable,

nodular (< 5 cm), and contain bedrock fragments. The nonpedogenic type is massive, homogeneous, layered, and tends to occur in paleo-drainage channels (Wheatly, 1978). Similar alluvial valley-fills and associated lake deposits cemented by calcium carbonate are widespread along the disorganised drainage systems of the Western Plateau, Western Australia. These calcretes are commonly up to 10 m thick and include friable as well as nodular types (Butt and Smith, 1980).

Wheatley (1978) examined pedogenic and non-pedogenic calcrete profiles developed over weakly mineralised amphibole schist near the Aggeneys-Gamsberg deposits in semi-arid Bushmanland (Fig. 7). Both profiles are overlain by 2 - 10 cm of red sandy loam with an alkaline reaction (pH = 8.5). The pedogenic calcrete, represented by the calcretised C-zone of the residual soil, is characterised by rubbly nodular calcrete hosting progressively more bedrock fragments down the profile (Fig. 74). The lack of bedrock fragments in the non pedogenic profile indicates this to be transported alluvium subsequently cemented by a lateral influx of carbonate. The progressive depletion of Cu, Ni, and Zn in the minus 80-mesh fraction, from bedrock to surface, in the pedogenic profile indicates limited dispersion. This is especially marked for copper which shows strong depletion in the top soil with respect to bedrock. The relative immobility of copper in this alkaline calcrete environment is caused by the precipitation of malachite in the weathered bedrock under moderate to high pH, by HCO3/OH- exchange (Andrew, 1980) :

 $2Cu^{2+} + 3OH^{-} + HCO_{3}^{-} = CuCO_{3} \cdot Cu(OH)_{2} + H_{2}O$.

In the case of the non-pedogenic profile, surface soil values bear no relationship to bedrock mineralisation (Fig. 74). Recognition of the two calcrete types is therefore critical in planning and interpreting regional soil surveys.

Calcreted soils have a neutral to alkaline reaction. If the pH of hydrolysis (Fig. 5) is the only parameter limiting element mobility in calcretes, we would expect a relative order of depletion of metal ions in surface soils overlying calcrete-covered mineralisation (least to most depleted) : Mn < Ag < Zn < Ni < Pb < Cu (where < reads : is less depleted than). In the natural enviroment, many chemical and physical variables such as insoluble carbonate formation and metal complexing may rearrange the elements in the above sequence. From Fig. 74 the order in the Aggeneys study is Ni/Pb < Zn << Cu.



Figure 74. Pedogenic (endogenous) and non-pedogenic (exogenous) soil-metal profiles over amphibole schist with disseminated copper mineralisation. Note upward dispersion of metals through pedogenic profile and total lack of correlation between surface and bedrock chemistry in the non-pedogenic profile. (From : Wheatley, 1978).

The surface expression of the Copperton volcaongenic massive sulphide (Cu-Zn) deposit, 55 km southwest of Prieska (Fig. 7), was investigated by Beeson *et al.*,(1975). The ore zone is vertical, narrow (\sim 10 m) and subcrops on the extensively peneplaned Post African surface (Fig. 73) which is coincident with an extrumed pre-Karoo surface (Andrew, 1980). The upper 100 m of the zone has been leached during a wet paleo-climate leaving scattered gossan rubble (≤ 4m) and amphibolite as the only surface expression of the zone. Calcretisation and silicification of the upper 1 - 3m of the friable gossan are the result of a more recent arid climate.

Beeson *et al.*, (1975) show that the total extractable Cu, Pb, and Zn of the minus 200-mesh fraction of the surface soil clearly outlines the subcropping ore (Fig. 75). Soil values greater than 1½ times background for Pb, Cu and Zn extend downslope for 100, 250, and 650 m respectively. Calcrete samples, analysed for Cu and Pb, returned higher absolute values but dispersion is limited to 50 m (Fig. 75). Beeson *et al.* concluded that regional sampling using surface soils or calcrete should employ 200 or 50 m sample spacing respectively to detect mineralisation in this environment.

Cox, (1975), examined residual soil profiles containing up to 1.5 m of calcrete over Ni-Cu mineralisation at Pioneer, western Australia (Fig. 76). The soils are developed on a deeply truncated laterite profile. He found that systematic sampling and analysis (hot acid) of the minus 80-mesh fraction of the upper 10 cm of the pedogenic calcrete or the overlying residual solonised brown soil, gave welldefined Ni/Cr, Cu, and Ni responses over ultramafics and amphibolite, and very high anomalies over mineralisation. Zinc values are too eratic to be of direct value. Metal values in the soil and top of the calcrete are of the same order of magnitude and only mildly lower than those at the base of the calcrete. Cox concludes that soil sampling is an effective exploration technique in this environment.

From these examples it becomes clear that the contrast between anomalies over mineralisation and background is lower in topsoils and surface calcrete than in samples of bedrock or pedogenic calcrete immediately overlying bedrock. The contrast is less marked in the area examined by Cox (1975) since metal distribution in the profile largely reflects supergene processes of the wetter paleoclimate predating calcretisation. In southern Africa this contrast is generally much more extreme (Bradshaw and Thomson, 1979),

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Figure 75. Profiles showing distribution of Cu, Pb, and Zn in the minus 200-mesh fraction of surface (0 - 15 cm) soils (solid line), and in calcrete (dotted line), across the Prieska Cu-Zn orebody. Horizontal dashed line on Pb plot represents lower detection limit. Analysis by atomic absorption after nitric-hydrochloric leach

(From : Beeson et al., 1975).

and orientation studies are necessary to determine the sample medium, size fraction, and analytical technique that yields the most diagnostic mineralisation-related geochemical signiture. The study by Garnett *et al.*, (1983) at the Putsberg (copper) and Kantienpan (zinc) occurrences subcropping on the African erosion surface (Fig. 7) shows that even in this terrain where geochemical responses are subdued, well defined dispersion halos can be detected over calcrete-covered mineralisation.



- 1. Jimberlana Dyke
- 2. Kambalda
- 3. Lake Yindarlgooda
- 4. Mt Keith

- 5. Perserverance
- 6. Pioneer
- 7. Spargoville
- 8. Stuart Shelf area.

Figure 76. Australia case history locality map showing distribution of climatic regions, using the Köppen system. (From : Mabbutt, 1980). The Putsberg deposit (Fig. 7) is located on the African surface (Fig. 73) and occurs in a complex synformal zone of aluminous and graphitic schists, metaquartzites and amphibolites which overlies the basal gneisses of the Bushmanland Sequence (Campbell and Mason, 1979). The calcrete layer in the vicinity of the ore zone averages 1 - 2 m in thickness and comprises an upper zone of calcrete boulders (≤ 50 cm across) underlain by fine-grained amorphous calcrete. The boulder calcrete may grade laterally into both nodular (1 - 5 cm nodules) or finer calcrete. The base of the calcrete is indistinct while the top is sharp, overlain by about 20 cm of buff coloured sandy soil grading to orange-red at surface. The soil probably contains a significant aeolian component. Scattered gossan fragments occur throughout the profile.

Garnett *et al.*, investigated both vertical and lateral metal dispersion across the mineralised horizon. Samples were collected from the soil and the top and base of the calcrete. Several size fractions were analysed by atomic absorption after a hot perchloric-nitric-hydrofluoric digestion (Fig. 77). Median values were calculated for Cu, Pb, Zn, Ni, Co, Mn, Cd, Ag, Ba, and Cr for the various size fractions and expressed as a percentage of the median value for that element in rock chips taken from the base of the calcrete. Since the median value for an element in the rock chips is taken as 100 percent, all other median values for that element in other fractions can be compared with this to give figures for percentage enrichment or depletion (*op cit.*).

Results (Fig. 77) show that Cu, Pb and Zn tenor decreases progressively up the profile and with increase in grain size within each zone. The silty fraction of the soil and top of calcrete returning the highest values. Manganese, like Cu, Pb, and Zn shows a depletion of values with increase in particle size, but is enriched in the fines. The high mobility of Mn²⁺ in alkaline solutions (Fig. 5) permits wide dispersion, with the clay fraction representing a precipitation barrier. This loosely adsorbed manganese oxide is probably the source of the desert varnish coating the larger surface pebbles. The scavenging action of manganese may also in part, be responsible for the fixing of Cu and Zn in the fines fraction. Cadmium and silver are depleted in the surface soil and appear to concentrate preferentially in the coarser fraction. Barium and chromium, like Cu, Pb, Zn and Mn are concentrated in the finer fraction but show only mild depletion in the surface layers.

Position	Fraction	n	Copper	Lead	Zinc	Manganese	Cadmium	Silver	Barium	Chromium
Soil	1 to 2 mm 75 to 180 μm	43 43	3 8	10 14	7 18	40 118	00	0	37 54	44 85
Top of calcrete	5 cm boulder calcrete 1 to 5 cm nodules 2 to 10 mm calcrete chips 1 to 2 mm 75 to 180 µm	52 38 38 43 43	6 9 11 4 11	16 19 27 21 24	8 11 17 13 19	4 48 58 60 108	97 117 100 0 - 0	55 50 60 0 0	70 76 74 69 86	71 68 76 71 129
Base of calcrete	5 cm boulder calcrete 1 to 5 cm nodules 2 to 10 mm calcrete chips 1 to 2 mm 75 to 180 µm	15 39 40 43 43	5 19 23 20 24	15 28 45 38 20	3 24 31 44 39	29 39 46 65 65	117 125 133 166 166	60 105 110 40 100	106 129 127 101 200	62 68 76 82 114
	2 mm rock chips	43	100	100	100	100	100	100	100	100

Figure 77. Median base-metal tenor in different size fractions from selected horizons in the Putsberg soil profile expressed as a percentage of base of calcrete rock chip median metal values. (From ! Garnett et al., 1983).

Even though copper is severly depleted in this surficial environment, both the 1 - 2 mm and 75 - 180 μ m fraction of both soil and top of calcrete clearly define the subcropping ore zone. Downslope dispersion is noticeable in the soil but not in the calcrete samples (Fig. 78). Calcrete samples however, yield higher absolute values. Fig. 79 compares the response of the soil and the top of the calcrete for zinc in the 75 to 180 μ m fraction. Anomaly contrast is much higher for the top of the calcrete than for the soil. Contrast can be improved if the dilutant effect of the calcium carbonate is removed by means of an ammonium acetate leach before total analysis is carried out on the residue (Fig. 79).

Barium shows a strong negative anomaly over the mineral-

isation with well defined highs over foot- and hanging wall lithologies. (Fig. 80).



Figure 78. Putsberg trench : copper response in soil and top of calcrete for the 1 - 2 mm fraction (1), and the 75 - 180 µm fraction (2). Solid black bars represent location of mineralisation below the calcrete. (From : Garnett et al. 1983).

Results of a drainage survey over the Putsberg mineralisation show that only copper yields short dispersion trains of 200 and 150 m for the 75 to 180 μ m and 1 - 2 mm fraction respect-ively.

These results show that characteristic geochemical signatures can be detected in the fine fraction of both soils and the upper calcretes over-lying base-metal mineralisation with anomalies in the top of the calcrete generally giving better contrast and higher absolute values. Drainage base-metal dispersion trains in calcrete environments are extremely short, unlike those detected by Beeson *et al.*, (1975), and McLaurin (1970), in streams draining the wellexposed Aggeneys (Fig. 58) and Gamsberg deposits (Fig. 52).

At the Kantienpan (Fig. 7) zinc occurrence, where extremely hard silicified calcrete (hardpan calcrete) either directly overlies mineralisation or is underlain by friable amorphous calcrete, the metal distribution in the profile is much the same as at Putsberg. Metal values are lower due to the intense calcretisation of the profile. Garnett *et al.*, (1983) recommend high density stream sediment sampling followed by soil or top-of-calcrete sampling as the best primary reconnaissance approach in this terrain.



Figure 79. Putsberg trench : zinc in the 75 to 180µm fraction : acetate leach compared with total assays for soil, leach residue, and top of calcrete. Solid black bars represent location of mineralisation below the calcrete. (From : Garnett et al., 1983).



Figure 80. Putsberg trench : barium geochemistry for the base of the calcrete for the 1 - 2 mm fraction (1), and the 75 to 180 µm fraction (2). (From : Garnett et al., 1983).

Exploration in Laterite Terrain - Western Australia

Ore deposits in arid Western Australia have had a long and complex history of subaerial weathering probably dating from the Mesozoic. A deep lateritic weathering mantle developed under the generally humid conditions during the Oligocene and Miocene. Lateritisation was not a single event however, as laterites have developed on surfaces of different ages. The predominantly granitic rocks of the Western Australian shield have weathered to give a characteristic profile 45 - 60 m deep which shows surface iron oxide accumulations over a pallid, kaolinitic saprolite zone. Over the more basic rocks the same principle is followed although mineralogy is more complex with more exaggerated ferruginous expressions and carbonate development (Butt and Sheppy, 1975). Rocks may be leached to depths of up to 100 m (Cox, 1975). The resulting silica cap and laterites present severe obstacles to base-metal exploration.

The objective of studying deep weathering profiles is to determine whether the weathered zones have characteristics that can be used to indicate the nature of the parent rocks. In particular, in the case of ultrabasic rocks, it is helpful to distinguish between barren rocks and those rich in Ni-sulphides. It should be remembered that deep lateritic weathering can itself concentrate Cr, Co, Ni, and Cu, regardless of the presence of primary sulphides (Butt and Nickel, 1981).

The lateritic profile has subsequently been altered and variably dissected during the succeeding arid and semi-arid periods. Considerable geochemical variablility is thus introduced in the surficial environment not only by difference in primary mineralogy but also by geomorphic setting. (Fig. 81). Consequently, geochemical signatures indicative of subsurface mineralisation are applicable to restricted topographic units that have undergone a similar weathering history and show the same amount of profile truncation. Conventional geochemical procedures involving the sampling of rocks, gossans, stream sediments and soils are only applicable in pedimented areas (Fig. 81) where outcrop, whether of fresh rock, saprolite or residual soil, occurs. Elsewhere, carefully controlled sampling and analytical procedures following thorough orientation work are employed to detect bedrock mineralisation.



Figure 81. Idealised section showing some of the major landforms developed over Archean rocks in inland Western Australia. (From : Butt and Sheppy, 1975).

Preserved Laterite Profiles

Nickel sulphide mineralisation in the Archean greenstone belts of the Yilgarn Block of the Precambrian shield of Western Australia occurs as high-grade massive sulphides in stratiform volcanic ultramafic assemblages or as low-grade disseminated sulphides in intrusive dunitic bodies. Several techniques have been documented to discriminate between nickel gossans and ironstones and siliceous material of similar appearance, produced by deep lateritic weathering of rocks of minor nickel content. Methods rely heavily on the detection of pathfinder elements present in the strongly leached profile in abundances greatly in excess of that in false gossans.

Hot acid-extractable Cu, Ni, and Cr and the Ni/Cr ratio have been successfully used in areas of thin residual overburden developed on deeply truncated laterite profiles to

locate and distinguish between barren and mineralised ultramafics at Pioneer (Cox, 1975) and over the Jimberlana Dyke (Mazzucchelli and Robbins (1973), (Fig. 76). Similar conclusions were reached by Mazzucchelli (1972) who showed that nickel sulphide mineralisation at Kambalda (Fig. 76) gave rise to well-defined Ni/Cu anomalies in the minus 80-mesh fraction of the residual soils that are free of the masking effect of laterite. Butt and Sheppy (1975) assayed drill chips from bores over disseminated mineralisation in the Mt Keith area (Fig. 76), located on the old plateau beneath 90 m of leached and chemically altered overburden and found that anomalous acid soluble Cu and Ni in the profile usually but not always indicated mineralisation. They concluded that parameters other than simple Cu and Ni values and ratios are necessary to locate large disseminated Mt Keithtype Fe-Ni-Cu sulphide deposits.

Wilmhurst (1975) reported on extensive geochemical investigations carried out at Perserverance and Spargoville (Fig. 76) in deeply laterised terrain. They sampled massive and disseminated sulphide gossans, ironstones, various silicification products and weathered unmineralised ultramafics, and concluded that Pt and Pd are the only elements that consitently indicate Ni-sulphide mineralisation since these elements resist movement during weathering and leaching.

Clema and Stevens-Hoare (1973) studied a number of nickel sulphide gossans in the Yilgarn and devised successful empirical scattergrams which make use of various combinations and ratios of Cu, Ni, Zn, Pb, Mn and perchloricnitric acid-soluble Cr (Fig. 82) to distinguish true from false gossans. Similar diagrams based on Cr³ and Cu x Ni, and a triangular plot based on weight percent Ni, Zn and Cu are used by Moeskops (1977). Moeskops suggests that these plots are useful methods in the preliminary discrimination of true gossans and adds that Pt, Pd and Se values be determined to distinguish true gossans positively.



Figure 82. Signature diagrams of Clema and Stevans-Hoare (1973) designed to distinguish true from false massive nickel sulphide gossans with new data by Moeskops (1977). (From : Moeskops, 1977) (Note : Cr = perchloric-nitric acid-soluble Cr).

Travis *et al.*, (1976) demonstrated that Ir is not mobile during gossan formation and that the Ir content of gossans can be used to give a reliable estimate of the nickel sulphide content of unoxidised parent material. Similar conclusions are reported by Keays and Davison (1976), who also showed that barren ultramafic hosts are characterised by low Pd/Ir and Au/Ir ratios while nickel sulphide ores have high ratios. McGoldrick and Keays (1981) used the Ir
content in the deep weathering profile at Perserverance (Fig. 76) to assess the absolute mobility in the laterite profile of Au, Pd, Pt, Ag, Co, Cr, Se, Tl, As and Sb (by neutron activation) and Cu and Ni (by atomic absorption). The study showed that :

- (1) Co and Cu are lost from the upper 15 m of the oxide zone
- (2) Cu is probably retained during gossan formation
- (3) Cr, Au, Pt, and Pd are conserved during weathering, confirming the use of Pt and Pd (as well as Ir) as indicators of gossans developed over nickel sulphide mineralisation.
- (4) Ag is lost from the profile
- (5) Se is retained in the gossan close to the levels in ore, and may be used like Ir to indicate the grade of Ni mineralisation. Furthermore, the S/Se ratios in gossans developed over massive and disseminated ore of magmatic origin are generally much lower than ratios in gossans developed on sulphides of sedimentary origin (Stanton, 1972) although exceptions do occur.
- (6) Tl is lost from the upper portion of the oxide zone. Although the Tl primary dispersion is weakened during oxidation it still persists well above levels in false gossans.
- (7) There is a strong absolute enrichment of As and Sb in the oxide zone. Those elements (T1, As, and Sb) are strongly scavenged by iron oxyhydroxides.

The more important results are shown in Fig. 83.

Similar discriminatory techniques for other base-metal ores subcropping in latertic terrain have been devised (see Smith *et al.*, 1978, discussed under *gossans*).

Truncated Laterite Profiles

In areas where the laterite profile has been deeply truncated, conventional exploration methods have been successfully used and have already been mentioned earlier (see : Cox, 1975 ; Mazzuchelli 1972 ; and Mazzuchelli and Robbins, 1973). The upper iron oxide horizon may be eroded, exposing silcrete or hardened saprolite. Recognition of the level of truncation is important since the strength of geochemical responses varies with position in the profile (Fig. 83). The relative proportions of volatile and precious metals in the profile decrease with depth (Fig. 83) but are still anomalous with respect to barren oxide cappings. These elements thus remain useful indicators of mineralisation regardless of the level of erosion of the laterite profile.



Figure 83. The generalised enrichment-depletion trends for precious and volatile metals in the top 40 m at the Perserverance deposit. (From : McGoldrick and Keays, 1981).

The next International Geochemical Exploration Symposium, to be held at Perth, Western Australia, May 23 - 26 (1983) titled "Geochemical exploration in arid and deeply weathered environments" should provide an up to date review of current trends of exploration in these terrains.

CONCLUSIONS

The arid weathering environment is dominated by mechanical rather than chemical breakdown of minerals, hence tracemetals in the regolith are dispersed largely as little-weathered clastic grains.

Base-metal dispersion trains in streams decay rapidly to background due to dilution with barren material. Excellent results are obtained with the minus 40-mesh fraction. Dilution by wind-borne sand may be overcome by discarding the minus 80-mesh fraction. Clastic dispersion trains may be further enhanced by analysis of various magnetic and nonmagnetic fractions of panned concentrates.

In rugged terrain talus and stream sampling offers rapid geochemical cover. Thin stony soils in areas of moderate relief give good geochemical resonses. Optimum mesh size and extraction technique depends on the degree of aridity and the amount of calcium carbonate in the profile. Even severely calcretised or laterised residual soils reflect bedrock mineralisation.

Aridity enhances vapour migration within the regolith and ore-related volatiles absorbed onto soil particles are sample media offering deep geochemical penetration. Hydrogeochemistry, geobotany, biogeochemistry and surface microlayer analysis, are techniques applicable to areas of deep transported overburden and are in need of development before they may be applied with confidence. Trace element content of termite mounds appears to reflect bedrock mineralisation in areas of aeolian cover, while that of desert varnish seems to have little potential in geochemical exploration.

Geomorphological terrain mapping enables classification of various erosion surfaces, each recording geochemical processes related to past climates. Since arid weathering has little effect on trace-element dispersions within these paleo-regoliths, each surface has its own optimum geochemical exploration technique.

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APPENDIX 1

DETERMINATION OF pH ON SOIL, STREAM SEDIMENT OR PERCUSSION CHIPS (from Fletcher, 1981 ; Krauskopf, 1979).

1. Moisten soil/stream gravel with distilled water, consistently using the same water to soil ratio. (Fig. 84). This reduces the effects of pH fluctuations due to interactions of hydrogen ions in original pore water with those released from added water and their combined effect on soil colloids. In a more time-consuming procedure, the soil is brought to its moisture saturation point by careful addition of water until the surface of the wet soil glistens.

Treatment (soil : water)	pH	
	soil A	soil B
1:0.5	-	8.1
1:1	4.8	8.1
1:2	4.9	8.2
1:5	5.1	8.5
1:10	5.0	8.6
1:2 .01 M CaCl ₂	4.3	7.3
1:25 1.0 M KCl	3.9	8.3

Figure 84. Effect of soil to water ratio and the presence of salts on estimation of pH (From : Fletcher, 1981).

Determine pH of slurry. Occasionally different pH values are obtained depending on whether the reference electrode (but not the pH electrode) is placed in the soil suspension or in the clear supernatent liquid. This phenomenon, known as the *suspension effect*, can be avoided by consistently keeping the reference electrode at the same depth in the supernatant solution.

To avoid changes in electrode response due to scratches, robust electrodes protected by a plastic sleeve are most useful for measurements in soil slurries.

Note that previously dried soils, especially those containing fresh sulphides, may yield pH values 2 - 3 pH- points lower than the *in situ* value, due to partial oxidation of sulphide to sulphate. If soils are to be dried (before transportation to the laboratory or field camp), gentle air-drying is recommended as large temperature changes in the sample may cause a gain or loss in volatiles and related change in pH.

Be especially careful with alkaline (desert) soils as these may start off with a pH of 9.9 and on interaction with the atmosphere (loss of CO_2), pH may drop to 8.4 at equilibration with the atmosphere.

2. Moisten sample with a salt solution, for example, 0.01M calcium chloride (Fig. 84). This has the advantage of approximating soil-water composition for many soils. This reduces ion exchange effects and the system is much less susceptible to changes of solution to soil ratios. A disadvantage is that it is not possible to continue with the same solution and determine its conductivity.

Determine the pH of the suspension (note precautions mentioned in method 1 above).

APPENDIX 2

SUGGESTED METHOD FOR CALCULATION OF ELEMENT CONCENTRA-TION IN STREAM SEDIMENT AFTER PANNING HAS BEEN EMPLOYED - ANALYSIS BY X-RAY FLUORESCENCE.

- Be consistent in sample site selection. For example : sample only heads of longitudinal or point bars. Composite several smaller samples from a small area.
- Collect and weigh a constant volume of dry sample, say
 5 litres = M₁ g, which contains unknown concentration of C₁ ppm metal X.
- 3. Remove the +35-mesh fraction (> ½ mm) to reduce grainsize variation and improve pannability and limit the effect of composite grains in the concentrate. (Hallenstein, et al., 1981).
- 4. Pan down carefully until a chosen index mineral (quartz, feldspar) is largely removed. Dry and weigh concentrate. The following discussion assumes analysis will be carried out on a 20 g pellet, which is a common XRF requirement - see : Fletcher, 1981, p. 189.
 - (a) If concentrate < 20g add chemically inert filler
 (quartz) to make up a standard mass exceeding
 20 g = M₂g.
 - (b) If concentrate > 20 g, recovered mass = M_2g .
- 5. Submit M_2 fraction for analysis. C_2 = ppm metal X determined by XRF in fraction M_2
- 6. Determination of C_1 :
 - (a) In case 4(a) above, where amount of concentrate > 20 g : $C_1 = \frac{M_2 \times C_2}{20 \times M_1}$ ppm metal X.

(b) Where concentrate recovered was < 20g :

 $C_1 = \frac{M_2 \times C_2}{M_1}$ ppm.metal X.

Note that not all minerals behave similarly during panning. Some (like molybdenite) are panned away while others with good cleavage (galena) will be finer grained than the bulk of the sample and largely winnowed out during panning. The XRF value of C₁ calculated above, does not reflect the true concentration of that element in the original sample, but can be compared in a semiquantitative way, with values from similarly collected samples.

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