



The development of regolith exploration geochemistry in the tropics and sub-tropics



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ABSTRACT

This essay traces the development of geochemical exploration from its early beginnings in the modern era during the 1930s, concentrating especially in its application to deeply weathered terrain in the tropics and sub-tropics. Following promising results obtained in temperate regions in North America and Europe, test orientation surveys were conducted to see whether similar procedures were applicable in the tropics, where conventional geological prospecting was largely precluded due to the extensive cover of a deep lateritic regolith and consequent lack of outcrop. After initial work in Sierra Leone and Nigeria, the emphasis transferred to East Africa in the 1950s and 1960s, aimed principally at Cu exploration. Many of the basic principles for exploration in dominantly residual, free-draining terrain were quickly established in this period. Exploration in terrains with more complex weathering histories, however, raised a number of difficulties due to leaching and secondary concentrations of elements, problems in selecting and identifying appropriate sample media, and extensive transported overburden. These were encountered especially in more arid regions in Australia and Africa during exploration for Ni and Au during the 1970s and 1980s. This led to a change in approach, placing weathering and geochemical dispersion in the context of regolith and landscape evolution – a return to the early concept of landscape geochemistry. The 3D expression of mineralization in the landscape is depicted as empirical conceptual models, that account for both relict features and active processes, and portray element associations, dispersion mechanisms and host materials. They also indicate suitable sample media, sampling intervals and procedures for analysis and interpretation.

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1. Introduction

The principles of geochemical exploration have been known since the earliest days of humankind's quest for minerals, whether these were for tools, domestic use, worship, adornment, hunting or weapons. Initially, this involved tracing fragments of scattered ore to their source and, alternatively, as for gold and tin, seeking locations where they have been re-concentrated as alluvial deposits. The earliest systematic prospecting probably took place in the Neolithic period (4000–2400 BC in Europe, but from 9000–6000 BC in most lower latitude continents), seeking outcrops of various types of quartz, jade and even native metals (e.g., copper, meteoritic iron) for tools and utensils. Then, at different times across the globe, the Neolithic passed gradually into the Bronze (4000–1800 BC) and Iron (1500–500 BC) Ages, as the use of fire led to the development of metallurgy, humans became familiar with the elements gold, silver, copper, tin, iron, lead, antimony, mercury, platinum group metals, sulfur and carbon, as well as some of their compounds. Prospecting accordingly broadened to a wider range of minerals and metals and used different observations in the search, such as colored stains and ochres in float and streams, and the use of geobotanical

indicators. The actual methods were poorly documented, even in Greek and Roman times (Sagui, 1930), although Pliny (77 AD: R.W. Boyle, unpublished manuscript, 2003) mentions tracing mineralized float, panning for gold and cassiterite, and that soils overlying sulfide deposits were barren of plants. In China, geobotany was used before 500 BC for agriculture, to identify different types of soils and their suitability for crops, and for prospecting: plants indicating silver, gold, copper and tin ores were documented between 300 BC and 300 AD, and accumulator plants, including a type of purslane from which mercury could be extracted, were recorded by 1000 AD (Temple, 2013). Thereafter, few further developments in prospecting took place until the sixteenth century. Even then, Agricola (1556) and Boyle (1666) mostly described long known procedures using rocks, soils and plants, but due to the gradual improvement of chemical tests (Caley, 1979), Agricola added the examination of natural water, springs and water residues as guides to ores. However, it was not until improvements in analytical procedures in the late nineteenth and twentieth century that there was any significant use of geochemistry in exploration.

Widespread, systematic use of chemical analysis of soils, weathered rocks and, later, stream sediments in mineral exploration commenced in the 1930s (see Levinson, 1974, pp 4–9). The first such 'metallometric' surveys, for base metals and tin, were carried out in the former USSR,

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building on the fundamental work of geochemists such as V.I. Vernadskii and A.Y. Fersman. Smaller surveys were also conducted in Scandinavia and the UK at about the same time, based on independent work by V.M. Goldschmidt (Hawkes, 1976), with a bias towards biogeochemistry. Biogeochemical sampling undertaken over Cu, Au and Mn mineralization in Queensland, Australia, in 1939–1940 showed promise, but was suspended due to the war (Gaskin, 1950). The first trials of geochemical soil surveys in North America were commenced in the USA by the USGS in 1947 (Levinson, 1974). These included a range of different environments, with, in the early 1950s, apparently successful industry application in higher relief areas in the Pacific northwest and the southern Appalachians. Similar surveys were undertaken by Federal and Provincial Geological Surveys in Canada at about the same time, although extensive glacial overburden, especially in regions of low relief in the Canadian Shield, limited their success.

These initial surveys, including others in Europe, were dominantly undertaken in humid temperate regions. However, British and French investigations also extended to the tropics, due to their considerable colonial interests, especially in Africa and south east Asia. British Colonial Geological Surveys and the Geochemical Prospecting Research Centre (GPRC; later the Applied Geochemistry Research Group, AGRG) at Imperial College, London, worked extensively savanna and rainforest terrains in West Africa (Nigeria, Sierra Leone), East Africa (Uganda and present-day Zimbabwe and Zambia) and the Malay Peninsula. Over 100 students graduated with higher degrees from the GPRC-AGRG in the two decades following its establishment in 1954. Many worked in tropical terrains, including 21 in Africa (Howarth, 2010). Similarly, from about 1955, French organizations commenced research and exploration in western and northern Africa, and South America (Brazil, French Guiana). These groups adopted and adapted the procedures developed in North America and Europe; soil and stream sediments surveys were used with success, although limitations in areas of low relief with deep weathering and/or transported overburden were identified. In Australia, the first geochemical surveys (using vegetation) were done in 1939–1940, and soil surveys were tested in 1947–1952, mainly in semi-arid terrain. These surveys were limited in scope and at a time when the mining industry was at a low ebb; interest in exploration, including geochemical exploration, did not increase until the ‘nickel boom’ of the mid 1960s (Butt and Mazzucchelli, 2010).

By the late 1950s, geochemistry had become an established exploration technique (see Hawkes and Webb, 1963, pp. 2–8). The USSR was by far the leading proponent, with geochemical surveys compulsory for State exploration organizations; their activities, especially in the deserts of Central Asia, greatly exceeded the total effort of all other regions of the world. There was also considerable activity in central and eastern Africa and expanding usage in Scandinavia, Ireland and N. America. During the 1960s, advances in analytical techniques permitted more rapid, precise and accurate acquisition of geochemical data, and the (mostly experimental) use of a wider range of sample media. At the same time, computer-aided techniques of data handling and statistical interpretation were developed, permitting rapid evaluation of the increasing volumes of information being acquired. However, as noted above, geochemical techniques were less successful in regolith-dominated regions of low relief. In northern Europe and Canada, glacial deposits of diverse composition and origin alter or obscure the surface expression of bedrock mineralization, whereas in tropical and sub-tropical regions, deep weathering and/or transported overburden have a similar effect. The recognition of these issues prompted the development of terrain-specific exploration techniques based on the concepts of landscape geochemistry.

Landscape geochemistry describes the distribution of chemical elements in a landscape in terms of (1) the materials in which they occur, at all scales, and (2), the chemical and physical dispersion mechanisms responsible for this distribution. It considers all processes that occur between the surface and the weathering front. Depending on their location, landscapes may develop over periods of 10^6 or even 10^7 years, and various components of the regolith within them over

10^2 to 10^6 years. Accordingly, landscape geochemistry not only describes processes active under the present environment but also those that have operated in the past. It is thus an appropriate basis for describing and interpreting geochemical exploration data, and data from other disciplines of environmental geochemistry. Landscape geochemistry was developed in the former USSR in the 1940s to 1960s (Polynov, 1937; Perel'man, 1961: cited by Bradshaw, 1975; Fortescue, 1975) to provide a geochemical basis for classifying and mapping terrain, using factors that control element dispersion, such as bedrock geology, soil type, climate and relief. These principles were adopted by Fortescue (1975) and Bradshaw (1975) to summarize geochemical exploration data in the form of Idealized or Conceptual models, using three-dimensional block diagrams of landscapes. These authors developed models for glaciated terrain in Canada, but similar approaches have subsequently been applied to the Basin and Range Province, USA and Mexico (Lovering and McCarthy, 1978) and to deeply weathered terrain in Australia (Butt and Smith, 1980) and elsewhere in the tropics and sub-tropics (Butt and Zeegers, 1992).

2. Exploration in tropical environments, 1949–1970

1. Pioneering research in Africa

Deeply weathered tropical terrains were an early focus for geochemical exploration, with investigations in a range of climatic conditions in western, eastern and southern Africa undertaken from 1948 (Webb, 1958; Hawkes and Webb, 1963). This was a particular interest of Dr. (later Professor) John S. Webb of the Royal School of Mines, who wanted to establish whether techniques developed in humid temperate regions with mostly shallow soils could be applied in these very different environments. He realized that conventional prospecting based on geological mapping and outcrop sampling was inappropriate and ineffective in area with little or no outcrop, as were then-available geophysical techniques. Initially, in 1949, Webb and PhD student A.P. Millman conducted orientation surveys over weathered Pb–Zn mineralization in Nigeria. They followed the ideas behind earlier work in Scandinavia and then ongoing research by H.V. Warren in Canada by emphasizing vegetation and groundwater sampling. Soils were also sampled in this and parallel studies by R.O. Roberts and H.E. Hawkes (Hawkes, 1954, 1976; Webb, 1958; Howarth, 2010). Results were generally positive, but were not followed up by further research.

Some of the earliest commercial applications of geochemical exploration in Africa were attempted by Roan Selection Trust (Services) Ltd. in the Zambian (then Northern Rhodesian) Copperbelt in 1952, but were hampered by laborious sampling techniques, slow, unreliable analysis and erratic data (Tooms and Webb, 1961). Accordingly, the company then sponsored Webb to conduct formal research into appropriate techniques, commencing in 1953 with J. S. Tooms' PhD. The initial studies were mainly ‘proof of concept’ orientation surveys, aimed at demonstrating the existence of surface geochemical anomalies over sub-cropping mineralization, developing field (and laboratory) techniques for their detection and determining factors that might influence the interpretation of geochemical data. Sample media tested included residual soils, bog and seepage soils, deep weathering profiles, vegetation, termitaria, groundwater, stream water and sediments and heavy mineral separates. Because of this regional focus, much of the research in this period was aimed at Cu (and Co) mineralization, but other orientation studies were conducted (Webb, 1958):

to test As and Sb as pathfinders for Au mineralization in Uganda and Sierra Leone;
 over W and Mo mineralization in Uganda and Sierra Leone, respectively;
 over Sn and Nb mineralization in Uganda; and
 to investigate the potential of multi-element soil geochemistry for geological mapping.

Most of these tests were conducted at locations where the regolith was residual and freely drained, including sites where lateritic duricrusts were present, and were generally successful (Webb, 1958). Maximum Cu values in ferruginous or 'lateritic' B horizon soils were generally one to two orders of magnitude lower than in underlying mineralization, and surface soils were leached still further, but both gave broader targets than the mineralization itself. Poorly-drained organic soils, developed on shallow colluvium–alluvium in seasonal swamps were also found valuable, since they could accumulate metal (especially Cu) derived from mineralization several hundred meters upslope, and hence had application for more regional surveys (Fig. 1; Govett, 2010). Few studies were attempted where surface regolith units were transported, although Hawkes (1954; see Hawkes and Webb, 1963, pp. 194–5) had previously reported a Pb–Zn anomaly of probable biogenic origin in shallow (2 m) alluvium overlying buried mineralization at Nyeba, Nigeria.

These orientation surveys established the most effective sample, sampling intervals and analytical size fraction for a range of commodities. The most appropriate soil sampling horizons were soon found to vary according to the environment, bedrock lithology and mineralization sought. Important messages were that the orientation should be thorough and as well-documented as possible, and that during exploration, the different soil horizons should be targeted, rather than sampling at specific depths. However, given that environments and soils vary across the landscape, the sample site and type should be recorded so that where these are markedly different, the data could be treated separately. Sample patterns and intervals were based on the size and shape of the recognizable dispersion halo from mineralization, such that ideally at least two lines traversed the anomaly and at least two samples fell within it (Hawkes and Webb, 1963).

The analysis itself was an issue. Most geochemical studies in the early 1950s used classical analytical methods; these delivered highly accurate data but were very slow. Webb and other pioneering exploration geochemists realized that for commercial application, it was necessary to analyze large numbers of samples over short times scales, and that consistency in analysis, – i.e., precision – was more important than

accuracy (Thomson, 2010). Furthermore, the availability of data in the field was a valuable aid in directing sampling and for preliminary follow-up, so that simple, rapid methods for field use were important. Accordingly, existing methods were adapted for these purposes, sacrificing accuracy for reproducibility. Over the next decade, rapid colorimetric procedures for the analysis of over 25 elements were developed, commonly using quite primitive equipment, especially that for field use (Stanton, 1966; Thomson, 2010). 'Total' analyses (to 95–98%) were achieved by fusing samples (e.g., acid fusion with K bisulfate alkaline fusion with Na carbonate and K nitrate) or, generally less efficiently, by solution in concentrated acids, prior to separation of the desired element(s) and partition into the colorimetric reagent. Every tenth analysis was of a control sample, to monitor precision. Most of the methods permitted analyses of 60–100 samples per day, at precisions of 10–15% at the 95% confidence level (laboratory conditions), or 15–25% (field conditions), the latter achievable by relatively untrained personnel. For most common elements (e.g., Cu, Pb, Mo, Ni, Zn), useful detection limits of 1 ppm or better were possible, although for others, such as Hg (2.5 ppm) and Au (about 0.5 ppm), the techniques were insufficiently sensitive for exploration.

Weak extractants were used to determine loosely bound, or mobile, metals – such as ammonium citrate for cold extractable Cu; these were the forerunners of the current commercially available range of partial extraction analyses. In temperate and glaciated terrain, partial extractants were used with some success to differentiate between labile metal derived from sulfides and those more strongly bound in silicates. In deeply weathered environments, the ratios of 'extractable' to 'total' metal ($cxMe/Me$) were interpreted as representing the relative activities of near-surface weathering and dispersion processes (Fig. 1), rather than the more optimistic interpretation in recent years of labile metals derived from great depth.

Over time, the rapid field- and laboratory-based analytical procedures were modified as techniques improved. By the late 1960s, for example, atomic absorption spectrometry replaced colorimetric methods for element estimation, permitting multi-element analysis from a single digestion. However, papers in Turner (1982) show that in East Africa

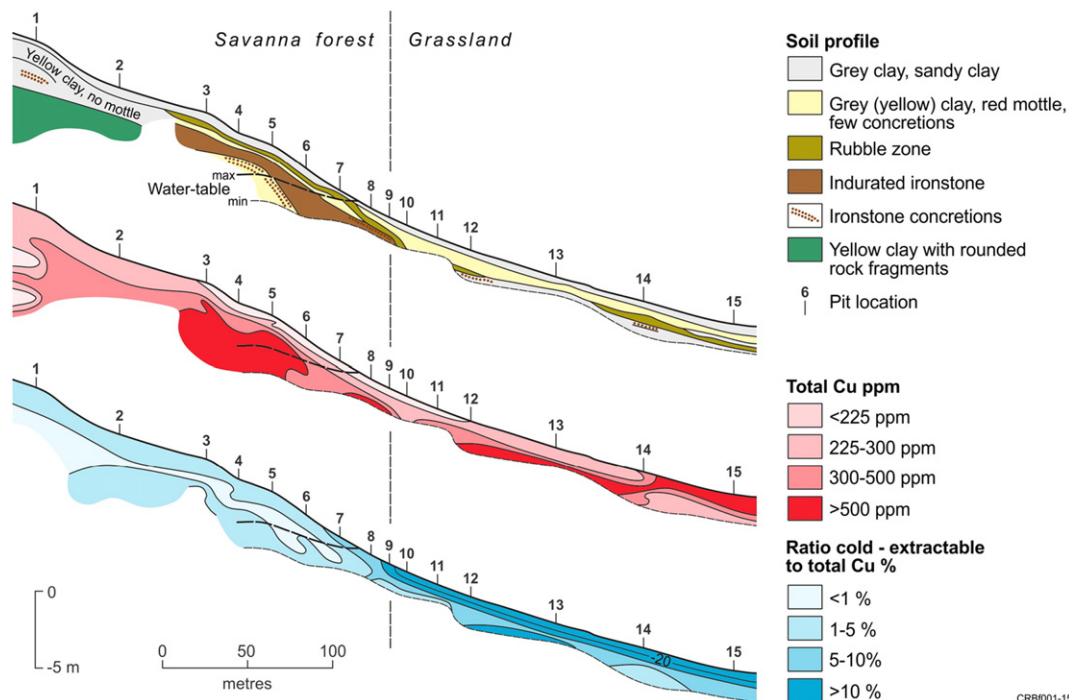


Fig. 1. Soil catena and distributions of total and the ratio of partially extractable to total Cu ($cxCu/Cu$) at Baluba, Zambia (after Govett, 1958, 1987, 2010). Copper is concentrated in the indurated Fe oxide-rich 'lateritic B horizon' in the free draining upland soils (savanna forest), whereas in the poorly drained lower slopes and seasonal swamps (dambos), it is concentrated in the organic A_0 horizon. The increased $cxCu/Cu$ ratio suggests this enrichment is hydromorphic.

the approach to sampling and interpretation remained largely unchanged for over two decades; a similar situation existed in most other deeply weathered terrains.

2. Misunderstood legacies

Two legacies of this early work that have been subsequently discussed and often misunderstood relate to the size fraction used for analysis and the concept of 'threshold' used to define anomalies. In most studies in both temperate and tropical regions, the minus 80-mesh (180 μm) fraction of soils and stream sediments was routinely used for analysis. Even now, more than half a century later, this remains a common 'standard'. The reason it was selected, however, was more pragmatic than based on rigorous experimentation: it is the optimal fraction to obtain and analyze without further sample preparation, important for rapid sample turn-round, especially in the field (Professor J.S. Webb, AGRG, personal communication, 1967). It is the coarsest fraction that will be readily analyzed by acid dissolution or fusion without grinding, and the finest that can be obtained quickly by dry sieving alone. It generally contains clays, fine heavy minerals, Fe oxides and Mn oxides, the probable hosts of dispersed target elements, but only small amounts of quartz, which is usually a barren diluent. Finer or coarser fractions may give greater abundances, higher contrasts or broader anomalies in specific circumstances, but the practical advantages of the minus 80-mesh fraction have prevailed for general use.

Determining the "threshold" value for defining element abundances that might indicate the presence of mineralization, i.e., the upper limit of background variation, has long been a matter of debate. Hawkes and Webb (1963) noted that orientation surveys may give a visual estimate based on elements dispersion patterns. However, in their absence, they considered that interpretation of exploration data should not rely solely on subjective appraisal but be supported by statistical analysis. They suggested as a practical measure, a threshold might be set such that it is exceeded by 1 sample in 40. This value can be established as mean plus two standard deviations for a single population, or, for multiple populations, the value exceeded by only 2.5% of the total sample population, with the median considered as mean background. These suggestions were purely arbitrary, because, clearly, any dataset must have 'anomalies' as defined by these threshold values even when no mineralization is present, but were offered as a means of formally presenting and analyzing geochemical data. With the subsequent advent of sophisticated computer analysis, coupled with the routine availability of multi-element data, and increasingly complex exploration environments, the concept of threshold is becoming less important, replaced by modeling of dispersion characteristics. Nonetheless, the conclusion of Hawkes and Webb (1963) that mathematical data interpretation has yet to replace the subjective talents of exploration geologists and geochemists is still valid.

3. Exploration in tropical and deeply weathered terrain worldwide

Geochemistry became widely applied elsewhere in tropical and subtropical regions in S. America, India, SE Asia and Australia from the early 1950s (Hawkes and Webb, 1963; ECAFE, 1963; Laming and Gibbs, 1982). Broadly similar techniques to those developed in West and East Africa were followed, but in places were adapted for local conditions, such as ridge and spur soil sampling in forested areas of high relief. There was a greater emphasis on stream sediment sampling as a reconnaissance tool in humid terrains, followed up by soil sampling in anomalous areas, whereas in semi-arid to arid terrain, soil sampling alone was employed. Although these procedures gave successful results in dominantly residual terrain of moderate relief (Bradshaw and Thomson, 1982), deep weathering and lateritization presented problems, due to the high degree of leaching of some metals from both soils and deeper regolith, but, in contrast, concentration of other elements in saprolite and/or ferruginous duricrust (Singh, 1982; Pollack

et al., 1982). However, apart from noting these variations and the influence of topography, little attempt was made to understand the reasons, many of which relate to the weathering and erosional histories of different regions and their influence on the nature and composition of potential sample media. This was demonstrated in Guyana by Gibbs (1982), who observed that the composition of stream sediments from lateritic uplands differed from those in sandy lowlands regions, the former being dominated by Fe oxide-rich fragments and having higher background concentrations of many elements.

Despite semi-quantitative procedures such as 'loaming', the systematic panning of soil samples for gold 'colors', being used successfully for over a century (Cash, 1959), geochemical techniques were slow to be adopted in Australia, with only a few studies across the continent prior to 1960. Exploration biogeochemistry was first formally trialed in 1939–1940 by the Aerial, Geological and Geophysical Survey of Northern Australia over copper, Au and Mn deposits in Queensland where subcropping mineralization at Dugald River affected vegetation assemblages (Gaskin, 1950). Subsequently, V.P. Sokoloff tested soil geochemistry at various locations in New South Wales and South Australia (Sokoloff, 1948, 1950, 1951). The Bureau of Mineral Resources (BMR, now Geoscience Australia) continued these investigations, principally in the Northern Territory and Queensland (e.g., Debnam, 1954a,b, 1960; Haldane, 1963), and local and regional variations in response were noted. For example, at McArthur River, NT, Haldane (1963) emphasized the importance of determining the origin of the samples selected for analysis: soils were effective in locating (sub-economic) Pb–Zn where developed on residuum, whereas in depositional areas, it was necessary to drill to the base of the alluvium to obtain suitable samples. Ruxton (1963) found that despite 15–25 m of weathering in the humid savanna climate at Rum Jungle, NT, leaching and dispersion of Pb and Cu in residual soil were only minor, whereas in the semi-arid Tennant Creek area, Cu was strongly leached in deep profiles and overlying soils, similar to the situation in Zambia (McMillan and Debnam, 1961, cited by Ruxton, 1963). Two of the first detailed geochemical research projects in Australia were PhD studies initiated by John Webb from the AGRG in 1962. A geochemical–geobotanical study re-investigated the Dugald River deposit (see above), and demonstrated that the distributions of characteristic plant assemblages was controlled by the abundance of toxic elements in soil (Nicolls et al., 1964). In the Eastern Goldfields of the Yilgarn Craton, W. Australia, Webb recognized that the geomorphology and regolith, especially the 'laterite' that mantled much of the bedrock, differed from those in regions he had studied elsewhere. R.H. Mazzucchelli followed up this observation during his PhD project. He established the use of As as a pathfinder for Au, in the absence of a suitable sensitive analytical procedure for Au itself, and pioneered the use of coarse ferruginous pisoliths and nodules as exploration sample media (Mazzucchelli and James, 1966). Gold exploration remained at a low ebb until the 1980s, but the understanding and experience of this project proved valuable during the surge of activity following the discovery of Ni sulfides at Kambalda in 1966. Initially, the prime geological/geochemical tool for Ni sulfides was gossan search, either directly for outcropping 'ironstones' or indirectly by using soils surveys to detect ironstone detritus. It soon became apparent that not all Ni-rich ironstones and soils were gossans or derived from gossans – and, conversely, that not all gossans and associated soils derived from Ni sulfides were Ni-rich. Secondary enrichment of Ni (\pm Co, Mn) to form low-grade Ni laterites over ultramafic rocks resulted in widespread 'anomalies' in saprolite, soils and ferruginous ironstones, whereas some gossans derived from Ni sulfides, especially those emplaced in felsic rocks, were highly leached. Considerable effort was dedicated to petrographic examination for sulfide fabrics, and to devising graphical statistical procedures for discriminating Ni gossans from gossans on barren sulfides and other ironstones, based on multi-element analysis. Discrimination was imperfect but nonetheless most of the principal deposits in areas of outcrop and residual soil were discovered at this time. Thereafter, the importance of gossan and soil

geochemistry for Ni exploration declined as the complexity of the regolith over much of the Yilgarn Craton prompted the use of drilling to sample bedrock in preference to surface media. The principal difficulties were a poor understanding of the landscape, the characteristics, evolution and very thickness of regolith, and their combined influence on the surface expression of mineralization.

3. Landscape geochemistry in deeply weathered terrain

As noted by Govett (1987), and tacitly recognized in the literature, it was not until 1974 that the influence of a long and complex history of weathering and landscape development on exploration geochemistry was first discussed in any detail. The impacts were exemplified by the geochemical expression in the regolith of disseminated Ni sulfide mineralization at Mt Keith, on the Yilgarn Craton of Western Australia (Butt and Sheppy, 1975). This was the commencement of a research program, still ongoing, to understand the mechanisms of geochemical dispersion within the context of landscape evolution. The research was initiated by CSIRO in Western Australia, aided by support from the mining industry, much through the Australian Mineral Industries Research Association (AMIRA International), but extended its scope across Australia under the auspices of the Cooperative Research Centre for Landscape Evolution (later Environments) and Mineral Exploration (CRC LEME). Rather than consider present conditions as a paramount to defining geochemical dispersion and hence exploration procedures, this research, from the outset, included the determination of chemical and mineralogical processes of weathering under different climatic conditions over time, the development of appropriate techniques for sampling, analysis and data interpretation, and mapping the 2D and 3D distribution of regolith units at a range of scales. The scope also included the formation of supergene and secondary mineral deposits.

The principal feature is the presence of a lateritic regolith, 30–100 m thick, generally considered to have formed under seasonally humid, probably tropical to sub-tropical conditions (i.e., savanna climate). Lateritization is mostly considered to have commenced in the Mesozoic, although late Palaeozoic dates have been recorded in places (Anand and Paine, 2002). The effect of such weathering has been profound alteration to the chemical and mineralogical compositions of bedrock, including mineralization, and their petrophysical properties. Subsequent changes in climate and/or tectonic conditions have modified this pre-existing regolith, but its presence remains the dominant influence on surface geochemistry.

Following the lead of Bradshaw (1975), the results of weathering and chemical dispersion studies in Australia have been placed in the context of landscape geochemistry, depicted as conceptual exploration models for a wide range of different geomorphological environments, supported by compilations of case histories (Butt and Smith, 1980; Butt et al., 2005; Anand and Butt, 2010). The models were initially classified according to the degree of preservation of the deep weathering profile, relief and the type of overburden (Table 1). They are largely empirical and summarize the case histories in terms of the nature and origin of the surface expression of mineralization, accounting for both relict features and active processes. The models portray element associations, dispersion mechanisms and host materials, and indicate suitable sample media, sampling intervals, and procedures for analysis and interpretation. They are intended to represent characteristics that may be common over quite wide regions. The models may direct, supplement or even replace further orientation surveys, the last option an important factor in exploration of poorly known terrain or for new styles of mineralization.

A similar approach was being followed in the savanna regions of sub-Saharan West Africa (Senegal, southern Mali, Burkina Faso and northern Côte d'Ivoire), mainly by researchers from French universities and research organizations. With an initial focus on the origins of the plateau landforms and the deeply weathered regolith and duricrusts developed on them, this work extended to implications

Table 1

Hierarchical classification of conceptual geochemical dispersion models for Australia (after Butt and Smith, 1980).

Case histories	Weathering profile	Landform situation	Type of overburden	Model
←	Complete weathering profile	A: Low relief ---	None	A1
			In situ	A2
			Transported	A3
	Partly stripped profile	B: Moderate relief	None	B1
			In situ	B2
			Transported	B3
		C: High relief ---	(May not exist)	
	Fresh bedrock	D: Low Relief ---	None	D1
			In situ	D2
			Transported	D3
	Partly stripped profile	E: Moderate relief	None	E1
			In situ	E2
			Transported	E3
	Fresh bedrock	F: High relief ---	None	F1
			In situ	F2
Transported			F3	
Partly stripped profile	G: Low relief ---	None	G1	
		In situ	G2	
		Transported	G3	
Fresh bedrock	H: Moderate relief	None	H1	
		In situ	H2	
		Transported	H3	
Partly stripped profile	I: High relief ---	None	I1	
		In situ	I2	
		Transported	I3	

for the development of secondary mineral deposits (e.g., bauxite) and addressed challenges posed to exploration for concealed bedrock mineralization (Michel, 1973; Zeegers and Leprun, 1979; Tardy, 1997). This research was boosted by the resurgence of gold exploration in the 1980s and was expanded to humid savannas and rainforests in Africa and S. America.

It was evident that broadly similar landscapes were present in deeply weathered terrains, especially on the continental landmasses between 35°N and 35°S. They occur in a range of present-day climatic regions, from rainforest to semi-arid and from tropical to temperate. The similarities in landforms and regoliths extend to similarities in the geochemical expression of mineralization. This realization led to collaboration between Australian and French researchers to compare and contrast geochemical dispersion characteristics across these terrains and regions, refining the exploration models (Table 2; Fig. 2) to highlight similarities and differences (Butt and Zeegers, 1989, 1992). The deep lateritic regolith has, arguably, comparable characteristics across these terrains, so the principal differences relate to climatic changes, either to more arid conditions, as in much of Australia and north Africa, or to more humid ones, as in the equatorial rainforests of S. America and Africa. In addition, tectonism, mostly epeirogenic in the continental landmasses, has led to erosion and, in places, significant relief inversion. Although this has resulted in partial removal of the regolith, in dry savannas and more arid areas, much of the detritus has remained in the landscape as a cover of transported overburden, masking the surface expression of mineralization. These more comprehensive models thus consider dispersion due to:

- 1: the initial periods of deep lateritic weathering;
- 2: modification of the deep regolith under changed climatic and/or tectonic conditions; and
- 3: the present climatic conditions.

Within a given area, the appropriate models can be established by regolith landform mapping. This was initially developed in the late

Table 2
Classification of geochemical dispersion models for tropically weathered terrains (after Butt and Zeegers, 1992).

Present climate	Savanna (seasonally humid; Aw, Cwa*) Rainforest (humid; Af, Am, Cwb*) Warm arid (BSh, BWb*)
(*Köppen classification)	
Modifications to pre-existing profile within each climatic zone.	
Pre-existing profile	A: Mostly preserved B: Partly truncated C: Fully truncated
Recent alteration	0: Minor 1: Low 2: Moderate 3: Strong
Recent accumulation, cementation or neoformation	0: None Al: Al oxides AS: Alsilicates Ca: Ca–Mg carbonates (calcrete) Gy: Gypsum (gypcrete) Fe: Iron oxides (ferricrete) Si: Silica (silcrete) Sm: Smectites
Overburden on pre-existing profile	0: None 1: Residual soil 2: Semi-residual 3: Transported
Examples:	
A*Ca[0,1]:	Lateritic residuum, with pedogenic carbonate; outcropping or beneath residual soil.
B*Si[3]:	truncated profile, silicified, transported overburden.
B**[3]:	buried truncated profile.
NB. An asterisk * is used for generalized models for which a characteristic is not diagnostic or identified.	

1940s as an agricultural management tool (as ‘Land System’ mapping) mainly for the Australian rangelands, although also applied in rainforests in Papua-New Guinea (see CSIRO Land Research Series, 2010). It is based on the premise that commonly there is a correlation between landform and the underlying regolith, so that mapped units can have a specific associations of landform, regolith materials, and, possibly, bedrock geology. A similar approach to classifying landforms and associated surface regolith materials was developed in West Africa by Thomas (1974), confirming the applicability of the models between continents. Interpretation of the factual maps can subdivide the landscape into broad regimes, depending upon the degree of preservation of an original, residual lateritic regolith. If the regolith is essentially ‘complete’, retaining

the uppermost ferruginous horizon, it forms the *relict* regime, whereas if partially or wholly eroded, it forms the *erosional* regime; if the residual regolith, either complete or truncated, is covered by transported overburden, it is mapped as the *depositional* regime. These are the same criteria that define the geochemical dispersion and exploration models. Specific sampling strategies apply in the different regimes, or mappable subsets of those regimes (Fig. 3), and it is essential to recognize this when planning geochemical surveys.

Clearly, the models are an oversimplification of a complex sequence of superimposed events. Nonetheless, they provide a framework for understanding the processes giving rise to the surface expression of bedrock mineralization and thereby suggest appropriate exploration procedures. They can also be applied to the formation of some secondary deposits. These attributes are illustrated by the following examples.

4. Some examples of landscape geochemical models

1. Gold dispersion and enrichment in deeply weathered terrain

Gold exploration has been one of the drivers of regolith research in Australia, Africa, S. America and India over the past 30 years. The results of numerous studies exemplify the similarities in the distribution of Au in the lateritic regolith in these regions; differences are related, in particular, to more recent changes in climatic and hydrological conditions (Fig. 4).

Gold shows only minor chemical mobility during lateritic weathering, concentrating in the surface ferruginous horizons mainly as a resistant mineral. It is, however, leached from the soil and upper part of the lateritic residuum, probably as organic complexes, and accumulates in the lower part and the immediately underlying mottled clay and upper saprolite, precipitated as very fine particles of secondary gold. The Au distribution is typified by the Kangaba deposit in southern Mali (Freyssinet et al., 1989a). Examinations of particulate Au show the primary grains (~15% Ag) in lateritic residuum are corroded, with Ag depletion rims, and that fine secondary grains (0%Ag) have precipitated with Fe oxides in the mottled clays. Lateral dispersion, probably largely mechanical, has resulted in a typical ‘mushroom’- or T-shaped distribution in the near-surface, giving a broad anomaly potentially detectable by widely-spaced sampling. There appears to have been little corrosion of Au in the saprolite and correspondingly little dispersion, although mass balance calculations suggest minor loss. In rainforest environments,

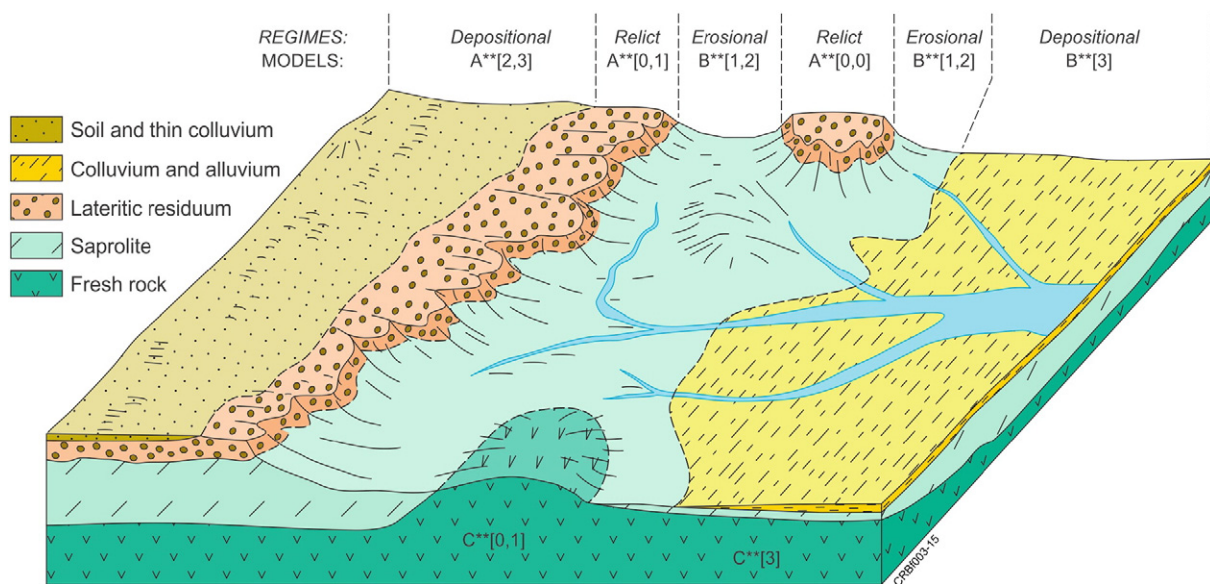


Fig. 2. The relationship between mappable regolith–landform regimes and geochemical models. Models codes (see Table 2) refer to the whether the lateritic regolith profile is A: preserved, B: partially truncated, or C: absent. The surface material is indicated as [0]: outcrop, [1]: residual soil, [2]: semi-residual soil and colluvium, and [3]: transported (after Butt and Zeegers, 1992).

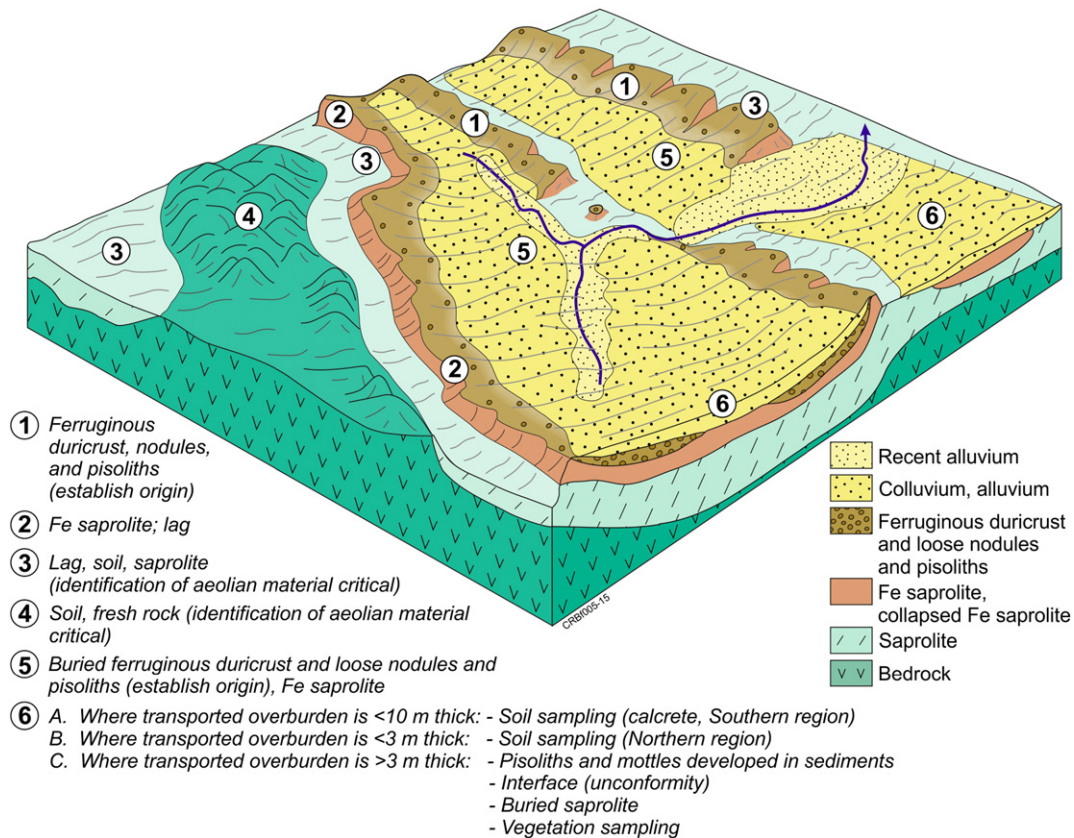


Fig. 3. Generalized regolith landform map, depicted as a block diagram, illustrating sample media appropriate for different regolith landform regimes. Based on experience in the Yilgarn Craton, Western Australia, the conclusions are appropriate for equivalent terrains elsewhere, although subject to local variations. After Anand and Paine, 2002; Anand and Butt, 2010.

pre-existing lateritic profiles are subjected to increased rainfall, so that corrosion and leaching of gold is more intense, but the overall Au distribution remains (e.g., Dondo Mubi, Gabon; Colin and Vieillard, 1991). Where lateritic residuum has been eroded (or never formed) and saprolite is exposed at surface, the lack of dispersion means that anomalies are very narrow, and surface leaching may result in them being of low contrast. Particulate Au in saprolite is also corroded, especially in rainforest environments (e.g., in Amazonas, Brazil, Larizzatti et al., 2008), in response to the greater leaching.

Gold distribution in complete lateritic regoliths in now semi-arid regions is generally similar to the original distribution exemplified by the present day savannas (e.g., Kangaba, above), except where the groundwater has become highly saline. Gold is strongly enriched in lateritic residuum but, unlike savannas, no surface leaching is evident, and high concentrations continue to the uppermost horizons and the modern soils derived from them. Physical and chemical dispersion can be extensive in lateritic duricrust, perhaps more so than in savannas, presenting an extensive exploration target (as noted under laterite geochemistry below), but again there is little or no dispersion in saprolite. Where groundwaters have become saline due to aridity, as in the Yilgarn and Gawler Cratons in Australia, Au is strongly leached from the upper saprolite to <100 ppb within the weathered ore zones, in places over a vertical depth of 40 m, and is reconcentrated in a sub-horizontal zone of supergene enrichment beneath. This enrichment is developed over the main mineralized zones and associated Au-bearing alteration haloes, and so does not represent lateral dispersion at depth. Both the lateritic and supergene enrichment zones contain abundant secondary Ag-poor Au grains (Freyssinet et al., 2005). Similar to savanna environments, where the lateritic residuum has been eroded, mineralization in saprolite, whether exposed or buried beneath younger sediments, presents a very narrow exploration target. Where it has been leached by saline groundwater, there may be essentially no expression in the

upper saprolite, other than in associated pathfinder elements such as As, Sb, Bi and W (e.g., Hannan South, Lawrance, 2001). However, in most regions in Australia characterized by saline groundwaters, pedogenic carbonates are present as evaporitic precipitates in soil, including soil developed on lateritic residuum. The carbonates are being actively precipitated and preferentially concentrate Au. Gold has probably been mobilized biogenically in the near surface and accumulates in a highly soluble form in calcrete. This phenomenon was first noted in the late 1980s (Lintern and Butt, 1993; Lintern, 2001). Sampling calcareous horizons in soil was quickly established as the basis for exploration in areas of residual soil and shallow transported cover in the southern Yilgarn and Gawler Cratons, and has led to many discoveries in both regions. The Au is probably derived from remnant residual Au particles scattered within the root zone and can give an Au anomaly (5→250 ppb) even where exposed saprolite has been strongly leached. Gold is the only ore-related metal to concentrate in pedogenic calcrete. In summary, studies of Au distribution have demonstrated the dispersion processes that have operated as the regolith developed and evolved, during lateritization, during subsequent climatically or tectonically induced modification, and under present day conditions whether rainforest, savanna or semi-arid. This understanding has led to better exploration procedures and an improved ability to interpret geochemical data.

2. 'Laterite' geochemistry

Relict landform regimes are defined by the presence of lateritic/bauxitic residuum. 'Laterite' geochemistry uses the ferruginous components of the residuum (duricrust, pisoliths, nodules and derived lag) as sample media. This has been a very successful procedure in Australia, especially for regional to district scale exploration. Laterite geochemistry exploits the residual enrichment of resistant minerals associated with ore deposits and their lateral dispersion in the near surface,

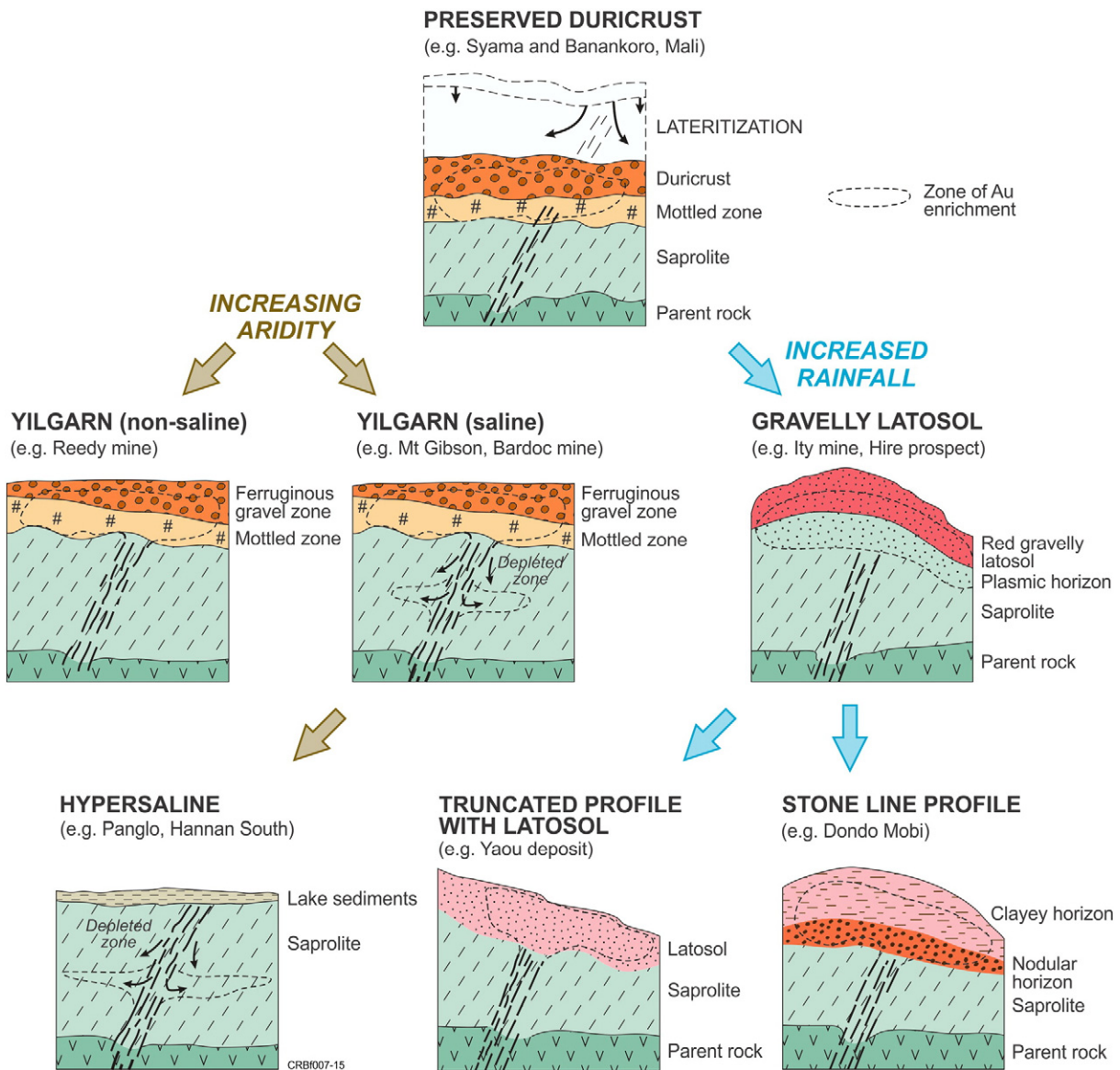


Fig. 4. Model illustrating Au dispersion during lateritization under humid savanna climates, and modification to Au distribution in the regolith due to subsequent climatic changes (after Freyssinet et al., 2005).

which may result in anomalies several times larger than the bedrock target. Gold may concentrate sufficiently to form mineable secondary deposits (see above). Laterite and lag sampling can define kilometer-scale anomalies surrounding base metal, pegmatite (Sn, Nb, Ta, Li, B) and Au deposits (Fig. 5; Smith and Perdrix, 1983; Carver et al., 1987; Smith et al., 1992; Anand and Butt, 2010), and at broad sampling intervals (3–9 km) can identify multi-element geochemical provinces (Smith et al., 1989; Cornelius et al., 2001, 2007). The same principles apply where lateritic residuum is buried beneath transported overburden, with samples collected by pitting or from drill cuttings, although especial care has to be taken to avoid sampling ferricrete (ferruginized sediment) and distally transported pisoliths and nodules.

Laterite geochemistry should also be applicable in relict terrains in other regions, as, for example, Cu is concentrated in sub-cropping lateritic duricrust in Zambia (Fig. 1; Govett, 2010) and Au enrichments and deposits similar to those in Western Australia are known in savannas, such as in Mali at Syama (Olson et al., 1992) and Kangaba (Freyssinet et al., 1989a), and in rainforests e.g., Rosebel, Suriname (Rapprechter, 2007). However, leaching in more humid climates reduces the surface response. Gold, for example, is leached from the near-surface and

deposited deeper in the lateritic horizon in seasonally humid Mediterranean regions in Australia (e.g., Boddington: Davy and El-Ansary, 1986; Anand and Butt, 2010) and in humid savannas and rainforests in Africa (Dondo Mobi, Gabon: Colin and Vieillard, 1991; Cassiporé, Brazil: Costa et al., 1993). Consequently, surface sampling of lateritic materials yields only weak, localized anomalies, markedly different from those in semi-arid regions, hence pitting or shallow drilling may be necessary to collect appropriate samples. Multi-element analyses might yield better results, as at Boddington, where pathfinder elements such as As, Bi and Sb remain anomalous at surface (Anand, 1994; Anand and Butt, 2010). A similar multi-element anomaly is described from Mborguéné, in the rainforest environment of Cameroun, where As, Au, Mo and Pb are broadly dispersed in the ferruginous nodular horizon (Freyssinet et al., 1989b), but the use of surface sampling was not investigated.

In West Africa, it is also possible that the ferruginous horizons capping the extensive plateau landforms have been mis-identified as lateritic residuum, whereas many may be ferricrete, i.e., ferruginized sediment. Tardy (1997) considered the landscape to have evolved conformably during post-Eocene uplift, and that the surface duricrusts are largely residual. However, it is evident that in many places these

Relict regime - lateritic residuum at or close to surface

Northern region: Non-calcareous soil, non-saline groundwater

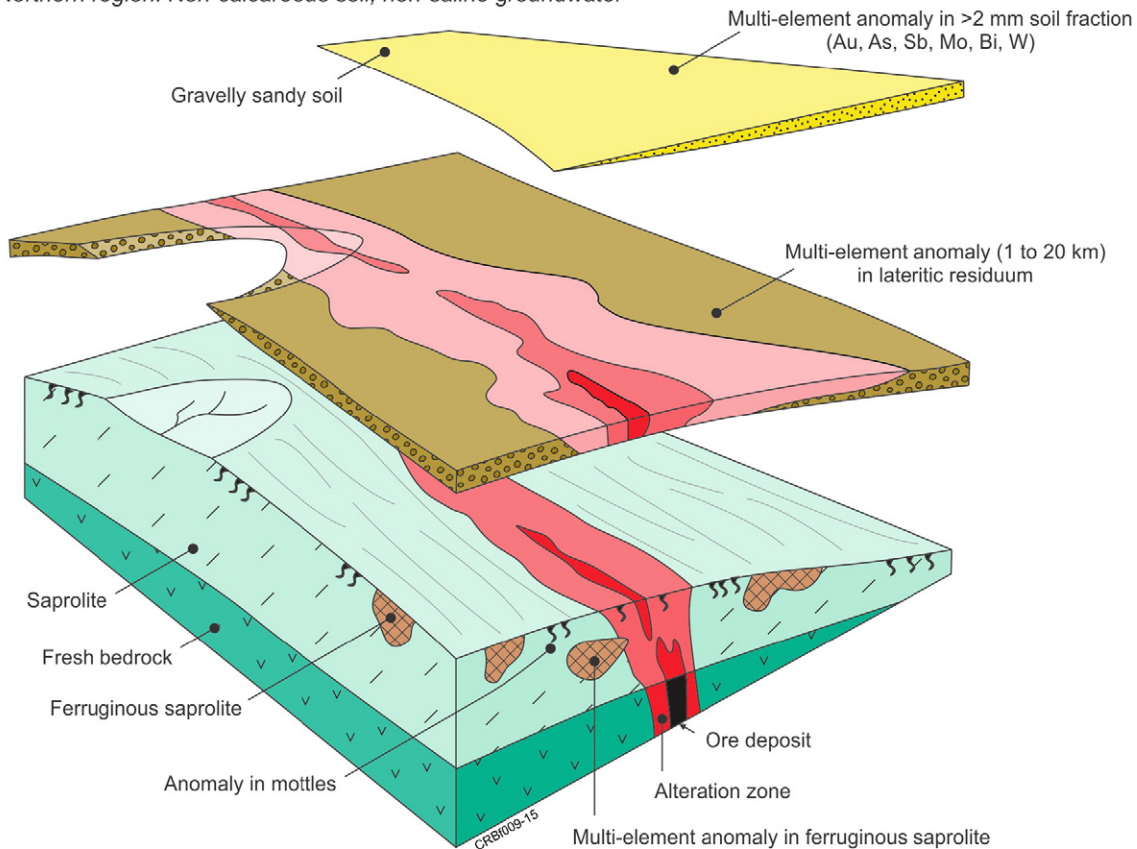


Fig. 5. Dispersion model for gold deposits where lateritic residuum is at or close to the surface in semi-arid regions of Western Australia having non-calcareous soil, non-saline groundwater. Similar models apply to base metal and pegmatite deposits, with different assemblages of immobile pathfinder elements (from Anand and Butt, 2010, after Smith and Perdrix, 1983; Smith et al., 1989; Smith et al., 1992; Butt et al., 2005).

duricrusts are ferricrete, and that the plateaux are products of topographic inversion (Bamba et al., 2002; Butt and Bristow, 2013, S. Bolster, personal communication, 2014). As such, although the landforms resemble dissected residual lateritic plateaux, they are part of a depositional regime, so that nodule and lag sampling will be ineffective.

3. Nickel laterites and nickel sulfide exploration

Most Ni laterite deposits are the products of several phases of development under changing tectonic or climatic conditions (Freysinet et al., 2005; Golightly, 2010; Butt and Cluzel, 2013). There are three main ore types (Brand et al., 1998), characterized by their mineralogy: *oxide ores*, (Fe and Mn oxides, with mean grades 1.0–1.6% Ni), *clay silicate* (smectites, e.g., nontronite, 1.0–1.5% Ni) and *hydrous silicate* (altered serpentine, 'garnierite', 1.5–2.5% Ni). Most deposits contain oxide and either hydrous silicate or clay silicate ore, although usually one type predominates. Nickel laterites are formed on ultramafic rocks, which generally contain 0.25–0.35% Ni hosted by variably serpentinized forsterite olivine. The initial stages of formation for most deposits was lateritization under dominantly humid savanna climates, with high, seasonally fluctuating water-tables and low erosion rates (Fig. 6A). In free draining environments on cratons and less active accretionary terranes, Mg and Si are strongly leached, with a total mass loss of up to 70%. In contrast, Ni, released by the hydrolysis of olivine or serpentinized olivine, is largely retained, hosted by goethite as low grade oxide deposits. In poorly drained environments, similar oxide deposits form on dunites, whereas on pyroxene-bearing peridotites leaching is less intense and Ni is mainly hosted by smectites. Tectonic uplift of areas of originally low relief rejuvenates the topography and lowers previously high water-tables. In the

humid tropics, this has typically led to leaching of Ni from the oxide zones and as weathering continues deeper in the saprolite, its concentration in hydrous Mg silicates. The latter process has formed the high grade ores of New Caledonia (Fig. 6B). Where there has been no significant uplift, but a change to more arid climates (e.g., in much of Australia), further development of Ni laterites is largely terminated, although precipitation of secondary carbonates and/or silica may dilute the ore or have implications for processing (Freysinet et al., 2005; Butt and Cluzel, 2013).

The enrichment processes that form Ni laterites similarly affect the ultramafic rocks hosting or associated with Ni sulfide deposits, hence lateritic terrains present particular problems to Ni sulfide exploration. There are commonly no significant differences in Ni abundances over barren or mineralized ultramafic rocks (Butt and Nickel, 1981), and secondary Ni enrichments may follow steeply-dipping structural elements such as shears, emulating the distribution of oxidized sulfide-rich units. The high Ni content of the weathered host rocks makes it difficult to recognize the signature of sulfides, whether at surface or deep in the regolith, and there are no consistent pathfinder elements, although Cu, PGEs and Te are commonly used. These features led to the complexities of gossan discrimination noted above.

Although it is generally assumed that sulfide oxidation and gossan formation are most active in humid, tropical climates, most gossans have been discovered in semi-arid to arid regions (Taylor and Thornber, 1992). It is possible that in the tropics, the Fe released from sulfides may remain in solution as organic complexes, or be redissolved from secondary oxides high in the profile, to become associated with ferrallitic soils developed over the wall rocks, rather than forming gossans that may later become indurated and outcrop. Accordingly, gossans may be poorly developed or absent in the upper parts of deeply weathered

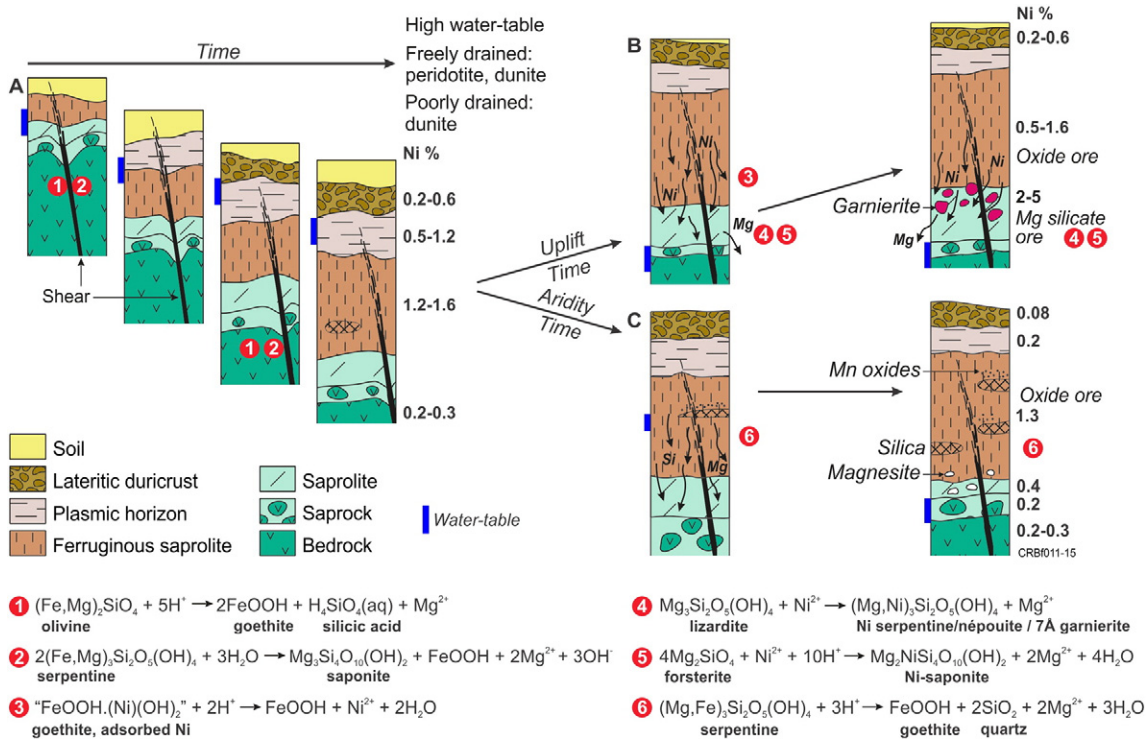


Fig. 6. Formation and evolution of oxide and hydrous Mg silicate deposits. (A) Progressive development of a well-differentiated lateritic regolith under a seasonally humid savanna climate in an area with low relief and tectonic stability. (B) With uplift and under a similar climate, leaching and reaction/exchange of Ni yield hydrous Mg silicates. (C) The profile is modified during a change to an arid climate, with precipitation of magnesite and silica (after Freyssinet et al., 2005; Butt and Cluzel, 2013).

profiles, even in arid climates (Butt, 1995). There is little direct evidence that gossans will not be present in such sites, but none appears to have been described to date. Dissolution and leaching of Fe may account for the absence of a gossan at the Harmony Ni deposit in Western Australia (N.W. Brand, personal communication), which was emplaced in felsic wallrocks weathered in an acidic environment. A similar process may also affect VMS-style Cu–Zn–Pb mineralization, thereby accounting for their seeming low occurrence in deeply weathered cratonic terranes.

4. Uranium deposits in calcrete and associated sediments

A landscape geochemical model of secondary U deposits in the northern Yilgarn Craton, Western Australia (Mann and Deutscher,

1978) succinctly summarizes the process of formation and indicates a potential exploration procedure using hydrogeochemistry (Fig. 7). These, and similar deposits in Africa and the Americas, have formed under semi-arid climates during the Pleistocene to Recent, with the U hosted by carnotite (K₂(UO₂)₂V₂O₈·H₂O) in groundwater calcrete and alluvial sediments in palaeodrainage channels. The cations are derived from the weathering of granitic rocks and transported to the valley axis in groundwater solution. They are concentrated by evaporation, with precipitation in confined sites controlled by prevailing redox conditions. Uranium is mobilized as uranyl carbonate complexes and V as a four-valent cation. Precipitation of carnotite occurs where concentrations have been elevated by evaporation and where V has been oxidized to the five-valent state. This may be where V has diffused upwards from

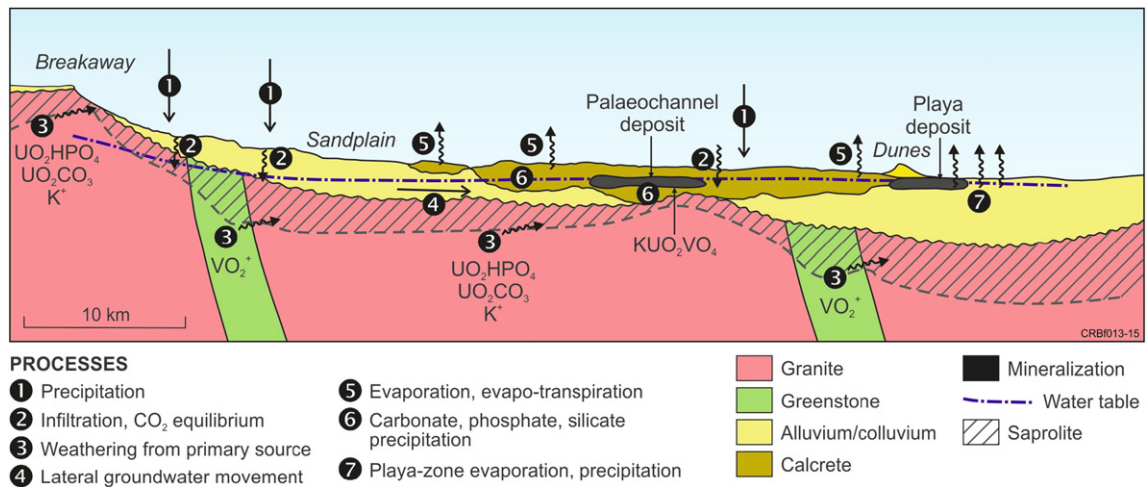


Fig. 7. General model of water–rock interactions and the formation of channel and playa secondary U deposit formation in the northeast Yilgarn Craton (Noble et al., 2011, modified from Mann and Deutscher, 1978). Uranium and potassium are derived from biotite and feldspar from granitic rocks; V may also be derived from ferromagnesian minerals in mafic dykes and greenstones.

depth under a redox gradient or where a subsurface bar has caused upwelling of groundwater into relatively oxidizing conditions. Changes in hydrological conditions over time, due to climate change or erosion, can cause changes in the sites of deposition in a drainage. Thus, in some localities, mineralization may be actively forming whereas in others, even in the same drainage, it may be dissolving. Hydrogeochemical surveys for U and V can indicate favorable regions and drainages for the formation of these deposits, but high values alone may not indicate where. However, the solubility index derived by Mann and Deutscher (1978) can be used to describe the hydrogeochemical status of a system with respect to carnotite mineralization, with decreasing undersaturation down drainage indicating proximity to a site of precipitation. Additionally, as carnotite dissolves incongruently, releasing vanadium, V concentrations in groundwater may increase down drainage from a dissolving deposit. Although radiometric surveys have been responsible for most discoveries, Gamble (1984) attributes one to hydrogeochemistry.

5. Summary and conclusions

Geochemistry has been applied successfully in mineral exploration in deeply weathered terrains since the early 1950s. Initially, it was used in dominantly residual regimes, principally targeting Cu and other base metals, but as sampling, analytical and interpretational procedures were refined, it was applied in areas of transported cover. In Zambia, for example, these ranged in character from seasonally swampy alluvium (Govett, 2010) to aeolian sands overlying lateritic regoliths (Brown, 1970), with the emphasis placed mainly on currently active dispersion into these units. It was recognized, however, that the overall secondary dispersion haloes developed over mineralization were the result of a succession of weathering events over time, and that these needed to be considered in order to optimize exploration procedures. In general, the effects of dispersion under the longest and most intense weathering episodes are retained, modified by the effects of tectonism on drainage status and overprinted by active dispersion under present conditions. Accordingly, since the mid-1970s, these considerations have been at the forefront of research and application in exploration geochemistry, the geology of supergene mineral deposits and in regolith research generally, with the processes considered in terms of landscape geochemistry.

The geomorphology and regolith of a region are the products of its weathering history and, hence, are keys to the dominant processes determining the geochemical expression of mineralization at each stage of the evolution of the landscape. A deeply weathered lateritic regolith is a characteristic of many regions in the present tropics and sub-tropics. Erosion during and following deep weathering, coupled with chemical and mineralogical modifications due to environmental change, has resulted in a mosaic of landforms in which the pre-existing regolith may be preserved or partly or wholly truncated, and either exposed or buried beneath transported overburden. The most important features of geochemical dispersion that occurred during the formation of the lateritic regolith include the strong leaching of most ore elements, restricted dispersion in the saprolite, and broad, multi-element haloes of immobile indicator elements in lateritic residuum. These features have been largely retained, irrespective of the present climate, although modified or overprinted during later weathering episodes. The nature of the geochemical expression of mineralization, and the availability and usefulness of specific surface and subsurface sample media thus vary across the landscape.

Regolith–landform mapping is an important first step to determining the appropriate geochemical exploration procedures. Mapping is based on the interpretation of a combination of aerial and satellite photography, satellite and airborne spectral imagery and radiometric surveys, with the third dimension supplied by airborne and ground magnetic and electromagnetic surveys, all supplemented by field inspection and, where available, drilling. The principal objectives include identification of the main regolith–landform regimes and, even at an informal level, establishing the probable dispersion processes and

optimizing sample selection and sampling procedures, sample interval, analytical procedures and element suites, and data interpretation, based on models developed from previous work in similar terrains elsewhere.

Although these basic principles are well established, numerous ‘cultural’ and technical issues restrict their application. The cultural issues relate to the stop-start nature of the exploration industry and its flow-on to research and education. Many of the advances in regolith geology and exploration geochemistry in deeply weathered terrain occurred during periods with high levels of exploration activity and strong support for research and teaching from universities, government institutions and industry e.g., in 1953–1965 (Africa), 1967–1975 (Australia), and 1986–2005 (globally). However, intermittent downturns between and during these periods led to losses of experienced staff in all groups and, especially recently, a decline in relevant courses, both undergraduate and postgraduate. As a consequence, proven, established procedures are now not being applied well, or even at all, and available information is not accessed or utilized.

Technical issues restricting the application of geochemistry relate to terrains that have received little research input by government institutions, universities or industry, due to physical or political access issues, and those that are dominated by transported cover. In some terrains, recognizing landform and regolith units can be challenging, especially for inexperienced geologists and geochemists, and, as every situation is in some way unique, district- and site-specific materials and relationships may be complex. On a broader scale, even in relatively well-studied areas, established basic interpretations may be incorrect, such as the plateau landforms of West Africa. As discussed above, the ferruginous duricrust (cuiresse) has been widely regarded as residual, whereas in many instances it has been shown to be transported (Bamba et al., 2002; Butt and Bristow, 2013), which has significant implications for understanding landscape evolution and using geochemistry for exploration in this region.

Transported overburden is a major hindrance to geochemical exploration in many deeply weathered terrains, ranging from the alluvial cover in the major river basins such as the Amazon and Congo, to the aeolian sediments in deserts and semi-deserts. In Australia, as much as 70% of prospective terrain may be concealed by transported overburden and sedimentary rocks of various ages. In the northern Yilgarn Craton, soil formed on only 2 m of colluvial cover may give no geochemical response to concealed mineralization. Sampling of transported overburden itself relies on detecting geochemical haloes formed by contemporaneous clastic dispersion of minerals containing ore-related elements or introduced by post-depositional chemical mobilization. However, few instances have been recorded or confirmed, other than at or close to the interface (unconformity) between the sediment and underlying residuum, where mechanical and/or hydromorphic dispersion have resulted in (usually weak) multi-element anomalies (Robertson et al., 2001; Anand and Butt, 2010; Anand and Robertson, 2012).

Many investigations have sought evidence for active dispersion through transported overburden. In various locations, targeted sampling of media such as termite mounds (e.g., Gleeson and Poulin, 1989; Petts et al., 2009; Stewart et al., 2012), pedogenic carbonates (for Au) (Lintern, 2001, 2015), vegetation and plant litter (e.g., Reid et al., 2008; Anand et al., 2007) have been shown to give a responses through 4 to 40 m of transported cover in certain environments. A summary of recent work in Australia investigating active dispersion by biological and gaseous vectors, set in a landscape context, is given by Anand et al. (2014). Gas and vapor geochemistry has also been investigated, mostly with negative or equivocal results, compounded by sampling and analytical problems. Dispersion mechanisms are poorly understood, but faults and fractures are major pathways and association with mineralization may be coincidental. Helium and Rn have been widely tested for U exploration but both give unreliable and commonly non-repeatable results, with numerous false anomalies and negative responses (or both) (Butt and Gole, 1985; Butt et al., 2000; Dyck and Jonasson, 2000). Mercury is mostly associated with solid phases (e.g., Fe oxides, organic matter) and is rarely dispersed as a vapor, hence is no more effective than other

pathfinder elements (Carr et al., 1986; Carr and Wilmschurst, 2000). Using activated C and kaolin gas collectors, Noble et al. (2013) suggested that a gaseous migration mechanism may be transporting Ni to the surface through 10–15 m of transported overburden over a weathered (~5 m thick residual regolith) Ni sulfide deposit in Western Australia, although the source of the metal (sulfides or ultramafic host rock) and carrier gas are uncertain. Groundwater sampling has promise both in regional surveys and in detecting 'near-misses' and research in this field is continuing (Gray et al., 2009).

Between 1990 and 2010, a proliferation of partial extraction procedures has been promoted on the premise of detecting active dispersion from mineralized sources. However, few if any verifiable case histories or discoveries have been recorded from terrains with deep weathering and/or thick transported overburden. In the semi-arid Yilgarn Craton, ten standard and proprietary partial analysis reagents were tested in soil surveys over several Au deposits (Gray et al., 1999; Anand et al., 2007). These studies showed that no reagent gave any advantage over total analysis, although they may give greater anomaly contrasts in places. No method (including total analysis) gave a detectable response through more than 10 m of cover. Partial extraction analyses might be expected to give better results in more humid area, where hydromorphic dispersion may be active, and over base metal deposits, which have a high concentration of potentially labile metals, but there are no definitive examples. In general, local features such as mineralogy, landscape position and overburden depth control the response and repeatability of different extraction methods. Many 'anomalous' responses detected by partial analysis are due to local chemical activity in the soil and are unrelated to mineralization, a conclusion reached by Webb and others in East Africa fifty years ago.

The successful application of exploration geochemistry in areas of transported overburden must continue to rely on understanding the geochemistry of the landscape. It requires a much improved knowledge of the geology of the sediments themselves, and the nature and timing of any post-depositional modifications. This will assist in determining if secondary dispersion haloes may be expected in the sediments and the most appropriate material to sample, or whether active dispersion may give a surface or near-surface response. However, exploration geochemistry has always proceeded through empirical testing of new or improved techniques, and the absence of detailed knowledge of the sedimentary cover should not preclude such experimentation – but the results need to be assessed rationally and not over-optimistically.

Conflict of interest

There are no conflicts of interest associated with the preparation or publication of this manuscript.

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