

Paper 1

## Major Advances in Exploration Geochemistry, 1998-2007

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### ABSTRACT

*Exploration geochemistry continues to be a major contributor to mineral exploration programs at all scales. The decade has spanned a complete economic cycle in the minerals industry, during which there has been a change in exploration emphasis from the dominance of Au and diamonds to the addition of a range of base metals and the recent revival of U exploration. Increasing metal prices and the development of new geochemical techniques have allowed exploration activity to expand in previously underexplored terrains, including those characterised by thick, transported regolith cover. There has been significant evolution and refinement of geochemical dispersion models for transported regolith, especially processes associated with oxidizing sulphide mineralisation. These models have prompted further developments in sampling methods, analytical techniques and approaches to anomaly detection. The routine measurement of fundamental soil and groundwater properties, such as pH, has been demonstrated to assist in detecting geochemical and mineralogical effects of buried mineralisation on regolith. New lithogeochemical techniques have been developed for terrane selection and early discrimination of potentially mineralised units. The production of regolith-landform maps, including 3-D models, and more detailed techniques for differentiating the origin and nature of regolith materials now underpins the design of exploration programs in a number of terrains. Various exploration techniques, such as biogeochemistry and soil gas, have been revitalised by the application of new technologies. Ongoing improvements to detection limits and the reliability of multielement analytical methods have permitted development and routine application of a wide range of selective geochemical extraction methods aimed at detecting subtle geochemical haloes developed in transported regolith cover. The results from a plethora of selective extraction orientation studies have, however, indicated the reliability of such methods to be uncertain, especially in arid terrains. Low-density geochemical mapping of large regions has been undertaken by government agencies for a variety of resource, environmental and health purposes, including attracting mineral exploration. Such maps typically demonstrate the dominance of underlying geology on regional geochemical patterns in regolith, even in industrialised regions. Philosophical and numerical approaches to defining and detecting geochemical anomalies continue to be reviewed. There is a need to supplement classical parametric outlier-detection approaches, routinely applied to geochemical data, with statistical techniques that reflect a recognition that subtle, multivariate patterns related to the geochemical effects of mineralisation may emanate from within the main data cloud and not outlying or distinct clusters. Future directions will likely include further convergence of exploration and environmental geochemistry and more substantial consideration of the effects of biological systems in understanding the processes involved in element mobility in the surficial environment. There will be an increased role for isotope analysis in terrane selection and mineralisation detection. An increasing risk to the technical capacity of the minerals exploration sector to discover new deposits is the progressive decline in the number of universities offering suitable geoscience programs.*

### INTRODUCTION

Exploration geochemistry continues to be a major contributor to mineral exploration programs at scales ranging from regional reconnaissance down to mining leases. Since the last decennial conference in 1997 the minerals industry has completed a full economic cycle and is benefiting from a surge in the price of most mineral commodities. The depressed markets of the late 1990s resulted in companies focusing exploration on locating

more resources in the vicinity of their existing mining operations, including the re-evaluation of old datasets. The current upswing has resulted in a return to greenfields exploration, including terranes with high mineral potential but which have been previously neglected or under explored.

The decade has provided various challenges for exploration geochemical research and applications. A technical challenge has been to develop methods capable of reliably detecting mineralisation covered by deep transported regolith, using the geochemical and mineralogical characteristics of surface

samples. New models for geochemical dispersion from deeply buried mineralisation have been proposed and new sampling and analytical techniques tested in a large number of orientation surveys, but with varying degrees of success. Another challenge has been the adjustment to changing commodity emphases, with the decade spanning the tail-end of the great Au epoch, the diamond rush and the base metal revival to a reawakening of U exploration, at a time when substantial exploration expertise has been lost from the industry (few practicing geochemists have had much experience with U exploration).

There has been some convergence between the disciplines of exploration geochemistry and environmental geochemistry, with the principal result being a number of multi-purpose geochemical baseline mapping programs, at regional to continental scales, being undertaken mainly by government agencies.

One fundamental geochemical question has survived six decades of debate: What constitutes a geochemical anomaly and how can this be enhanced (by suitable combinations of sampling processing and analytical methods) and detected (by use of various univariate and multivariate mathematical techniques)? This question has been revived again by the arrival of a variety of selective geochemical extraction methods linked to significant reductions in analytical detection limits. These methods have further revealed the complexity within geochemical landscapes, and the challenge of separating subtle geochemical signals related to the effects of mineralisation from the “noise” generated by the many processes that contribute to the overall geochemical and mineralogical characteristics of regolith.

This paper is intended to highlight some of the advances in exploration geochemistry over the last decade and point to developments for the next, rather than providing a comprehensive overview. A few of the key advances are expanded upon in other papers in this volume. As indicated by Closs (1997) in the previous decade, the ultimate objective of geochemical exploration is to assist the efficient discovery of ore deposits.

## TERRANE SELECTION AND TARGETING

Geochemical terrane modeling has proceeded along two lines:

- (i) lithogeochemical characterisation of environments conducive to the formation of mineral deposits and application of these methods on a regional scale in the early stages of exploration programs, to predict and subsequently select regions with potential for discoveries. Terrane targeting methods are not primarily used to “detect” specific mineral deposits, but to measure geochemical features consistent with processes that can lead to the formation of ore deposits. In many cases, the geology of these terranes may be poorly understood and reliable geological maps absent. Two examples discussed here are whole-rock lithogeochemical discrimination in volcanic arc terranes and the detrital zircon TerraneChron method; and
- (ii) evolution and geochemical characteristics of regolith and the development of secondary dispersion models upon

which mineral deposit targeting methods can be developed or refined. An example of this work is drawn from the arid terrains in Australia.

## Lithogeochemical Discrimination of Barren versus Fertile Intrusions

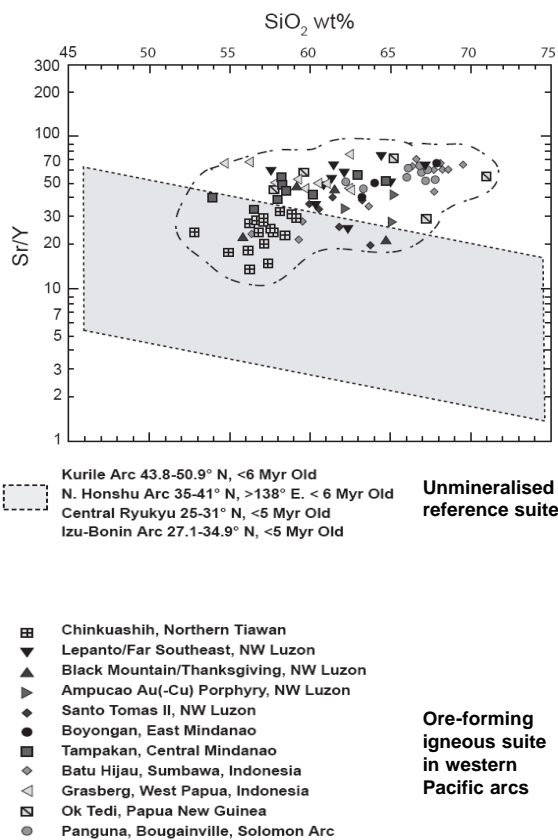
Porphyry Cu deposits can form from melts that undergo repeated cycles of replenishment by primitive magma and partial crystallisation (Rohrlach and Loucks, 2005). With each cycle, incompatible components, such as H<sub>2</sub>O, SO<sub>3</sub>, and Cl<sub>2</sub>, become progressively enriched in the residual melt, resulting in conditions that are optimal for Cu mineralisation. In the case of the Tampakan porphyry Cu-Au deposit in the Philippines, cogenetic silicic andesite has been shown to have increased water content in the melt (3–7.5 wt % H<sub>2</sub>O) over a 5 Ma period. This increased water content suppressed plagioclase crystallisation relative to hornblende, resulting in a significant increase in the ratio of the (plagioclase-hosted) Sr to the (hornblende-hosted) Y in fertile melts. Systematic whole-rock analysis of igneous rocks can, therefore, potentially discriminate fertile hydrous magmatic events. Application of this method to volcanic rocks derived from hydrous melts permits the regional assessment of porphyry copper prospectivity in arc terranes. Extensive reference suites of whole rock data have been compiled to compare “barren” terranes with “productive” terranes using Sr/Y versus SiO<sub>2</sub> (Figure 1). Although there is some overlap between the barren and productive suite, the productive suite tends to have elevated Sr/Y over a wide range of rock compositions.

## TerraneChron

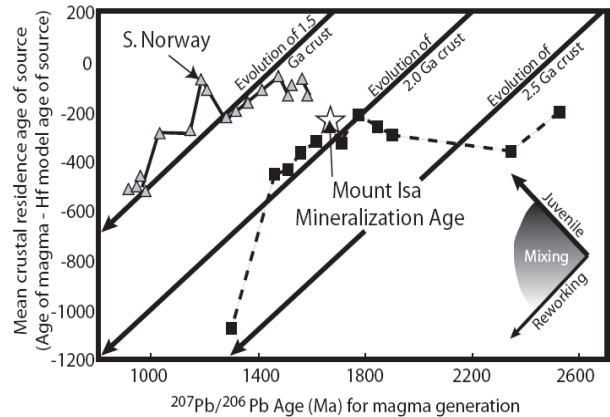
Zircons have long been used as a geochronometer, but their complex crystal structure also accommodates process-sensitive trace elements useful for understanding crustal development (Harley and Kelly, 2007). Because they are physically and chemically stable over long periods of time, they are preserved in regolith. The TerraneChron method integrates U-Pb dating, Hf isotopic analysis and trace element analysis of zircons obtained from drainage samples to characterise their source rocks (O’Reilly et al., 2004). Where applied over a large region, the method can provide an overview of the geologic history of a region and crustal evolution. The method is ideally suited for regional work where the geology is poorly known or correlating terranes separated by later tectonic events.

Isolation of different populations of zircons, based on size, color and chemical composition, allows different events to be characterised, including the age of formation, modelled ages of source rocks, the composition of parent rock types, and the source region for these rocks. The compilation of this information for a large number of zircon populations collected over a broad region is presented on an “event signature diagram”, which allows for interpretation of the crustal evolution for that region (Figure 2). The diagram shows the distribution of magmatic crystallisation ages for the zircon populations versus the mean crustal residence age of the source.

When pre-existing crust is being reworked (i.e., no new material is added), the results follow the evolutionary paths for crust at a given age (toward the lower left in Figure 2). When juvenile material is added, as might occur during significant compressional or extensional events, the results trend to the upper left, normal to the evolutionary paths. Hafnium isotopic results and rock compositions deduced from trace element data provide further insight into the tectonic events (e.g., rifting versus subduction) that have occurred. In the example, results for the Mt. Isa Eastern Succession indicate repeated extension and magmatism superimposed on an ancient crust. In contrast, results for southern Norway indicate continental build up of new crust at a continental margin with no indication of ancient crust. Characterizing well-endowed terranes with the TerraneChrom method may allow prediction of new terranes with potential for undiscovered resources.



**Figure 1:** Discriminant plot of Sr/Y versus SiO<sub>2</sub> showing rock suites associated with Cu-Au ore deposits (symbols) compared with a barren reference rock suite (shaded area) defined by hundreds of samples from northwest Pacific volcanic arcs, including intraoceanic and continental margin arcs. All analyses are from fresh or weakly altered (weakly propylitic at most) whole-rock samples. Modified from Rohrlach and Loucks (2005).



**Figure 2:** Example of an event signature diagram for detrital zircons from the Mt Isa (Australia) and southern Norway terranes (from O'Reilly et al., 2004).

### REGOLITH CHARACTERISATION AND EVOLUTION AND REGOLITH MAPPING

Regolith-dominated terrains pose considerable difficulties for exploration. Over the last decade such terrains have received considerable exploration attention as the potential for finding sizeable new mineral deposits becomes greater than in the more explored outcropping areas. This is largely due to a better understanding of all aspects of the regolith (its distribution, characteristics, processes and evolution) that are essential for effective geochemical and geophysical exploration program design. Much of this work is summarised by Butt et al. (2000), Anand and Paine (2002) and Anand and de Broekert (2005).

#### Regolith-landform Mapping

The importance of understanding the position of regolith materials within regolith stratigraphy and the landscape, for geochemical exploration, has become increasingly apparent in recent years. Regolith-landform mapping has gained greater importance and wider usage within the mineral industry over the last decade. Regolith features are an integrated expression of geology, climate, landforms, geomorphic processes and landscape evolution, and have close generic relationships with landforms. Thus, landforms become a surrogate for regolith and the basis of mapping. A crucial component of this mapping work has been reconciliation of observed regolith-landform relationships with carefully selected field traverses in each mapping unit (Pain et al., 2001; Anand and Paine, 2002).

Regolith-landform maps are not intended as end-products in themselves, but to provide two key pieces of information for mineral explorers – whether near-surface material is residual or transported, and the expected thickness of transported material. Both *factual* and *interpretative or derivative regolith-landform maps* have been produced for a number of terrains. Derivative maps are assisting in identifying probable dispersion models and subsequent design of geochemical surveys, including media selection, sampling procedures and intervals. Appropriate thresholds can then be set, anticipating and allowing for

variations in geochemical responses due to weathering or masking by transported cover. The likely effects of chemical and physical dispersion, resulting in displaced or transported anomalies, can be incorporated into data interpretation.

### **The Third Dimension**

Three dimensional regolith models are being built around large drill-hole datasets. For example, the Yandal project, in the Yilgarn Craton, included a 3-D representation of residual and transported regolith over a major gold system in an Archaean greenstone belt using a database of over 70,000 drill holes and high-resolution aeromagnetics (Anand, 2000) and spectacularly identified the maghemite-defined palaeodrainages. These 3-D models can define the base of the transported regolith, weathering fronts, internal regolith structure and have genuine predictive value. Although difficult to construct, due to inconsistencies in regolith logging and problems defining regolith unit interfaces, there have been advances in geophysical methods for regolith mapping methods that require minimal drill-hole calibration, including the low-frequency, broad-bandwidth, time-domain TEMPEST airborne EM system (Lane et al., 2000). With the advent of higher resolution aeromagnetic data, and the capacity to differentiate regolith features (e.g. Fe accumulation in palaeochannels) from bedrock magnetic feature, the interaction of drainage and geology becomes clearer. A significant observation from these transported regolith models is that, despite the subdued landscapes across much of Australia, the palaeotopography below the interface is quite rugged. It is this elusive form surface that will continue to host the most reliable direct geochemical indicators of buried mineral systems.

### **Landscape Evolution**

An understanding of the distribution and origin of regolith materials and palaeotopography have led to the refinement and development of new landscape evolution models in Australia and Africa (Bolster, 1999; Bamba *et al.*, 2002; Anand and Paine, 2002; Anand and de Broekert, 2005). These models have affected the interpretation of geochemical dispersion data and anomalies. Weathering profiles are recognized to have formed in both residual materials and also commonly in transported overburden of various ages (Figure 3). There have been several distinct phases of ferruginisation, deferruginisation, kaolinisation, silicification and calcification. The polyphase evolution of regolith has long been known but the advent of various geochronological techniques now permits quantification. The basic geochronological framework of the Australian regolith can be determined by palaeomagnetic dating using secondary hematite formed in saprolite by chemical weathering. Palaeomagnetic dates for regolith from 30 sites throughout Australia indicate two principal weathering events at around 10 Ma and 50-60 Ma, with some evidence of Mesozoic or even earlier weathering in the eastern Yilgarn and Cobar areas (Pillans, 2005). It is likely that each weathering event generates a new metal dispersion event, hence dating such events may

contribute to selection of more favourable geochemical sampling media - either bulk samples or mineral phases.

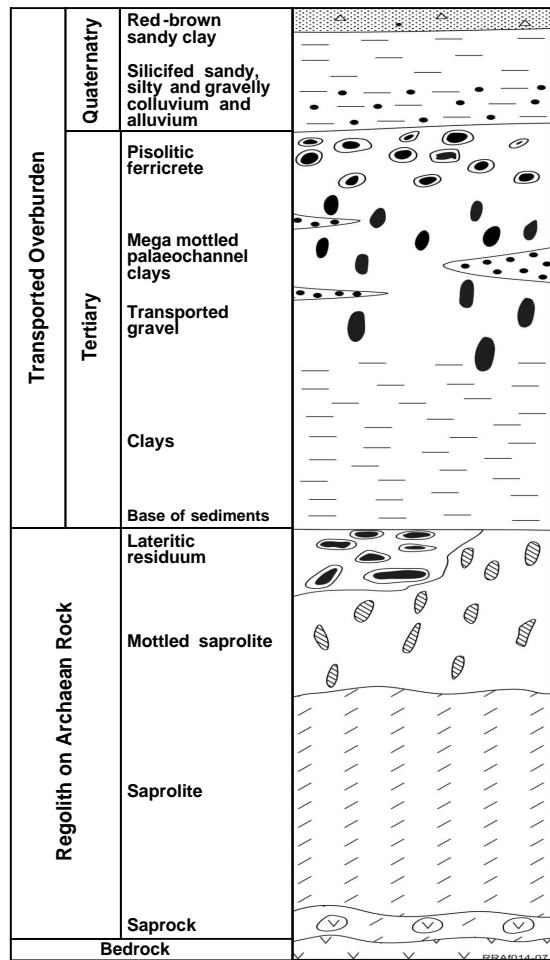
It is now clear that ferruginous pisoliths and duricrust have formed in a variety of materials including residuum, colluvium and alluvium. In places, ferruginous duricrusts occupy topographically higher areas due to relief inversion. Thus, a distinction between residual and transported types has been shown to be essential for geochemical sampling. Lateritic residuum forms largely by residual processes, hence elevated concentrations of Au and other elements in this material are generally the result of underlying deposits. Ferricretes are Fe cemented sediments and have been found to be generally unsuitable as sample media on a local scale but may contain indications of distal mineralisation, either within their detrital component or in the hydromorphically-derived goethite cement. Elements may be concentrated in ferricrete following lateral transport from sources that may be hundreds of metres to several kilometres away. Criteria have, therefore, been established to distinguish lateritic residuum from ferricrete (Anand and Paine, 2002).

### **EXPLORATION UNDER DEEP COVER**

Regions with thick, transported regolith or rock cover present special problems for exploration geochemistry approaches that use surface samples. Examples of such terrains include the northern parts of the Tasmanides in eastern Australia which are variably covered by thick alluvium and on-lapping Mesozoic to Tertiary sedimentary sequences, the Yilgarn Craton of Western Australia, the south-western USA and the Andes where thick gravel deposits fill the basins, and the recently glaciated terrains of the northern hemisphere with tills and glaciolacustrine sediments. Some of these regions have suffered under-exploration relative to their indicative mineral potential.

### **Dispersion Models**

Numerous case studies have documented the development of secondary geochemical dispersion haloes and mineralogical changes within transported regolith above deeply buried mineral deposits in various regolith setting (Mann et al., 1998; Lawrence, 1999; Wang et al., 1999; Smee, 1998; Kelley et al., 2003; Cameron et al., 2004; Butt et al., 2005). There is much debate on the mechanisms by which such dispersion proceeds, and these have included combinations of advection, groundwater flow, capillary action, diffusion of volatile compounds and biological action. Two mechanisms that have received significant attention over the last decade are electrochemical dispersion and cyclical dilatancy pumping.



**Figure 3:** Generalised regolith profile for the Yilgarn Craton, showing a three-layered strato-regolith architecture, each with different degrees of ferruginisation, probably relating to episodic weathering events.

#### Electrochemical dispersion

Self-potential currents, associated with oxidizing sulphide deposits, are the basis for one class of dispersion model in which the upward movement of electrons in an electrically conductive sulphide body results from the electrochemical gradients formed between (underlying) reducing and (overlying) oxidizing environments (Sato and Mooney, 1960; Govett, 1973; Bølviken and Logn, 1975; Smee, 1983). In all cases, the mass transfer of ionic species facilitates electrical current and the maintenance of charge balance, creating various types of geochemical anomalies in the overburden (Antropova et al., 1992; Goldberg, 1998). A revised model (Figure 4) provides for upward propagation of reduced species to the water table, forming a reduced column over the mineralised zone and the development of geochemical anomalies in the overlying surficial overburden (Hamilton, 1998, 2000). The oxidation of  $\text{Fe}^{2+}$  and its precipitation in ferric oxy-hydroxides causes acid production and subsequent dissolution of carbonate which precipitates at the edge of the reduced column where the pH is higher. Theoretical ion migration rates in electrochemical fields, linked to redox

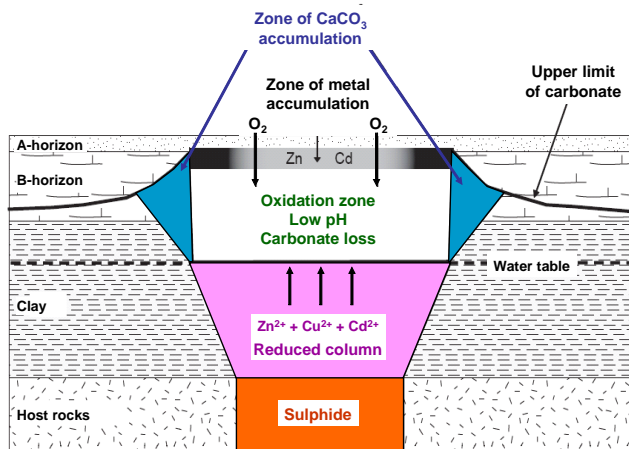
gradient effects, are much faster than diffusion rates and may permit the formation of geochemical anomalies at surface in young (~8,000 yr), thick, glacial sediments overlying mineral deposits (Hamilton, 1998; Hall et al., 2004). Given that  $\text{H}^+$  is the most mobile and one of the most reactive aqueous species, sustaining its presence over the reduced column in a high-rainfall, high-carbonate environment requires a continuous process (Hamilton et al., 2004b).

Several detailed investigations of surficial geochemical responses over deeply buried sulphide-hosted gold and VMS deposits in northern Ontario have been carried out by Cameron et al. (2004), Hall et al. (2004) and Hamilton et al. (2004a,b). Each of these studies characterised the pH, oxidation-reduction potential (ORP) and self potential (SP) in overburden and confirmed the presence of a reduced column above zones of buried mineralisation, as well as local zones of acidic groundwater, metal deposition,  $\text{CO}_2$  enrichment,  $\text{O}_2$  depletion, carbonate remobilisation, groundwater temperature anomalies and piezometric highs at the edge of the reduced column (Hamilton et al., 2003, 2004a, b). These features all support the redox-gradient model of Hamilton (1998, 2000). The piezometric highs may be a previously undocumented form of electro-osmosis, a process where fluid flow is induced by an electrical field (Hamilton et al., 2003). In addition, selective extractions and Pb isotope studies carried out in the VMS example (Hall et al., 2004) suggest that Pb was transported into the exotic overburden from the sulphides below.

#### Cyclical dilatancy pumping

Movement of metal-bearing groundwater surrounding mineral deposits is capable of redistributing metals both laterally and vertically. In areas with moderate to high relief and a shallow groundwater table, lateral, gravity-induced groundwater flow causes seeps to form at the base of slope where the groundwater table intersects the surface. Seeps produce hydromorphic accumulations of metals (mainly hydroxides), reflecting transport in reduced groundwater and subsequent atmospheric oxidation at the seep. Vertical migration of groundwater is more difficult, and requires an external energy source to propel water through the vadose zone. The expulsion of basinal fluids from sedimentary sequences undergoing active tectonic compression is well documented (Unruh et al., 1992). Saline perennial springs in the eastern margin of the northern Coast ranges, California, are caused by fluid overpressure zones in an actively deforming anticline in Upper Cretaceous marine shale and sandstone (Davisson et al., 1994). The discharge is a local phenomenon, with fluid migrating along fluid-pressure gradients and expelling along fractures and faults. Geochemical and geothermometry evidence indicates that the water expelled at an elevation of 230 to 380 m above sea level is dilute seawater that originated from depths of up to 4 km. The surface expulsion of groundwater from seismic activity is also well documented (Tchalenko, 1973; Nur, 1974; Sibson, 1981; Muir-Wood, 1994). In a process termed cyclical dilatancy pumping (Sibson, 2001), groundwater held in fractures is expelled during and after earthquake events. In extensional regimes, groundwater is held in open structures before the earthquake and is expelled during post-seismic compressional elastic rebound. In contrast,

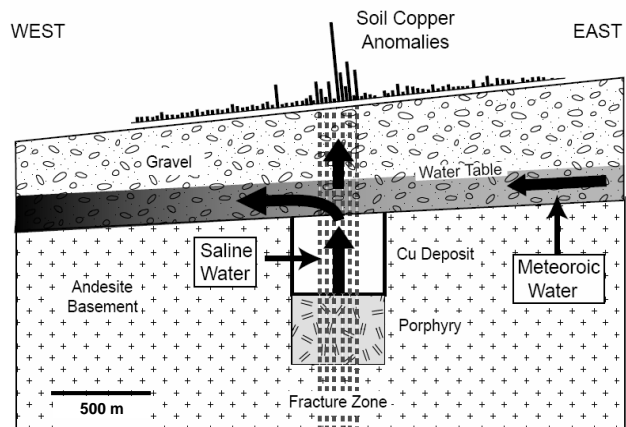
compressional regimes cause structures that are closed during pre-seismic time to open after the earthquake, increasing porosity and allowing water recharge. Hence, deep groundwater surrounding mineral deposits has the potential to disperse metals away from the deposit during seismic events.



**Figure 4:** Redox model from Hamilton (1998, 2000), modified after Cameron et al., (2004), showing development of a reduced column over sulphides in transported regolith. Metals mobile under reducing conditions migrate vertically along redox gradients. Above the water table metals are oxidised, creating a zone of low pH and carbonate loss. Carbonate precipitates at the edge of the reduced column. Metals such as Zn and Cd accumulate near surface.

Cameron et al. (2002) proposed that cyclical dilatancy pumping could explain the development of surface geochemical anomalies in areas with a thick vadose zone. Results of soil and groundwater analyses from an integrated study at the Spence porphyry copper deposit in northern Chile, which is buried beneath 50 to 100 m of Miocene gravels, are consistent with the vertical movement of saline metal-rich groundwater along fractures during earthquakes in this seismically active area (Figure 5; Cameron et al., 2002; Cameron and Leybourne, 2005). Copper in groundwater is restricted to the mineralised area due to the tendency of  $\text{Cu}^{2+}$  released by oxidation of sulphides to adsorb to Fe hydroxide colloidal particles and coatings, whereas elements that dissolve as anions (e.g., As, Mo, Se, and Re), are dispersed widely.

Field measurement of the conductivity of soil-water slurries showed two zones of salt (NaCl) enrichment, one directly over the deposit and the other 1 km away. Trenching of the soils in these zones revealed vertical fractures in the gravels, whereas trenching in a background area showed no fractures. The fracture zones appear to have formed by reactivation of basement faults. Elements present in the soils above the fracture zones are the same as those enriched in groundwater near the deposit and indicate redistribution of elements by groundwater movement to the surface during earthquakes, followed by evaporation and further



**Figure 5:** Conceptual model showing the generation of soil anomalies over the buried Spence porphyry Cu deposit, northern Chile. Vertical arrows show the flow path of deep saline waters during earthquake events along a fracture zone. Horizontal arrows show groundwater flow direction. Anomalous Cu in soil is interpreted to reflect injection of Cu-bearing saline groundwater into overburden following seismic events. Modified from Cameron et al. (2004).

redistribution by rain. Both fracture zones contain NaCl in addition to anomalous anions, whereas Cu is restricted to the fracture zone above the deposit. Additional evidence for the Cu anomalies in soil being related to cyclical dilatancy pumping comes from the presence of atacamite, a secondary mineral in the oxide zone of many deposits in northern Chile (Cameron and Leybourne, 2006). Atacamite is soluble in low-salinity water and would have been removed from the supergene profile had it formed as a primary oxidation product during supergene weathering. The composition of saline groundwater at Spence falls within the stability fields of the atacamite-brochantite assemblage and suggests that atacamite is the replacement of original copper oxide minerals by saline basinal fluids being pumped vertically through the deposit.

#### Alternate Sampling Media

In areas of transported regolith, a number of alternate sampling media to regolith are being evaluated. These include groundwater (Pirlo and Giblin, 2004; Giblin and Mazzuchelli, 1997; Kirste et al., 2004), soil gas (Highsmith, 2004; Polito et al., 2002; Rutherford et al., 2005) and vegetation (Cohen et al., 1998; Lintern, 2005; Dunn, 2007a,b; Anand et al., 2007). As with many of the new techniques being evaluated, interpretation of geochemical patterns in such media has tended towards the empirical rather than the mechanistic.

## REGIONAL GEOCHEMICAL MAPPING

### Regional and Global Baselines

Multi-element geochemical surveys, principally involving stream sediments or soils, continue to be a cornerstone of regional mineral exploration. The development of large-scale,

regional reconnaissance geochemical exploration surveys in the west originated with the NURE program in the USA (Gustavsson, et al., 2001), the NGR program in Canada (Coker et al., 1987) and the Wolfson Geochemical Atlas in the UK (McGrath and Loveland, 1992), and has continued into recent times with the geochemical mapping of China (Xie and Cheng, 1997; Li et al., 1999; Xujing, 2004) and other countries or provinces. These surveys were mainly designed to support mineral exploration.

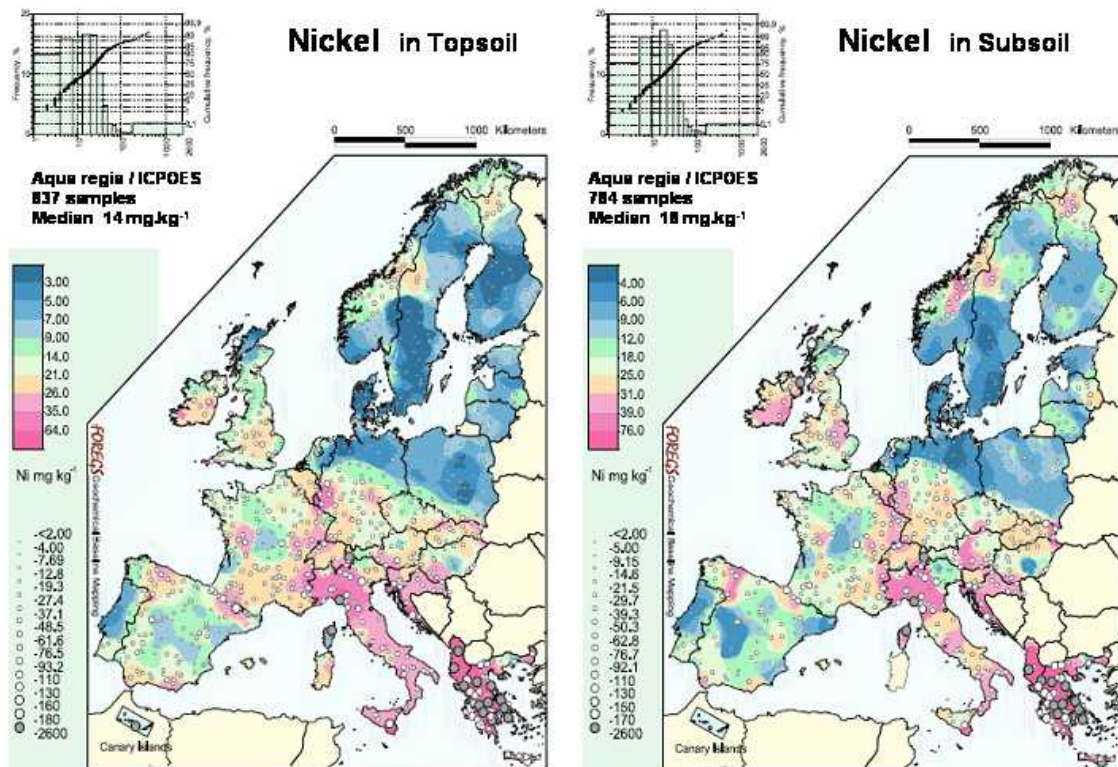
In post-mining and industrialised regions, such as Europe, regional geochemical surveys are now being undertaken for environmental monitoring, general resource planning and detection of sources of contamination (Volden et al., 1997; Plant et al., 2000, 2003). Following IGCP projects 259 and 360 (Global Geochemical Baseline; Darnley et al., 1995), a number of low density geochemical surveys have been completed in Europe. Part of this was prompted by a lack of information upon which to evaluate the impact of fallout from the 1986 Chernobyl nuclear disaster in Ukraine. The most recent release has been the FOREGS Geochemical Atlas of Europe (Salminen et al., 2006) in which ~800 sites were sampled for soils, floodplain sediments, stream sediments and waters, yielding a density of ~1 site per 5,000 km<sup>2</sup>. Despite 250 years of industrialisation (including smelting operations) and high variability in the nature of the regolith (from residual regolith to glacial sediments), the dominant control on most elements in the topsoil and subsoils is the underlying geology, with the example of Ni shown in Figure 6. This must have an impact on the definition of

“contamination” and in the setting of soil clean-up targets, given some regulatory authorities have set environmental action levels for trace elements in soils at industrial sites that are lower than natural concentrations (Salminen et al., 1998).

Apart from high quality data, such surveys can provide a valuable sample archive for future reference. The value of this is demonstrated by the recent production of a the National Geochemical Survey of the USA based on the multielement reanalysis of ~35,000 stream sediment samples collected in the 1960s under the NURE program (USGS, 2004).

### Role of Governments

The economic advantages gained by government investment in provision of pre-competitive exploration data, including geochemical maps, are agreed to by industry and geological surveys (Blight, 2002; Macdonald, 2002). Whereas the value of such databases has been demonstrated by the strong response to initiatives such as Discovery 2000 (Geological Survey of New South Wales), SAEI (Primary Industries and Resources of South Australia) and regolith mapping programs in Western Australia (Cornelius, et al., 2006), similar initiatives commonly founder when funding requests are considered by state or federal treasuries (Bowler, 2002). Provision of high quality, publicly-funded, geoscience databases reduce both the costs and the risks involved in greenfields exploration and target generation.



**Figure 6:** Comparison of aqua regia extractable Ni in topsoil (0–25 cm) with subsoil (50–75 cm) from the Geochemical Atlas of Europe (Salminen et al., 2006)

The value in such databases (though not necessarily the purpose in accessing) is indicated by the NGS survey where, over the last 30 months, there have been 5,000 browser hits (on individual web pages in the NGS), ~50 downloads of the complete dataset and ~65 customised datasets for specific regions or specific sets of samples (J. Grossman, USGS, pers commun 2007).

An associated task has been government support for the development of regolith and landform maps in countries such as Australia, which will form the basis for more rigorous sampling design and data interpretation in regional reconnaissance surveys (Brown, 2004).

## ADVANCES IN ANALYTICAL TECHNIQUES

### Multielement Analysis and Detection Limits

The wave of developments in selective geochemical extractions, and the implementation of large-scale geochemical surveys using these methods, has largely ridden on the back of developments in analytical methods, including the progressive lowering of routinely achievable detection limits, reduction in real costs and improvements in the reliability of analytical devices such as ICP-MS. Some new exploration techniques, such as the use of ultra-trace stable isotopes, have also been made possible by the availability of high resolution analytical devices such as multi-collector HR-ICP-MS. For many elements, routine detection limits for geochemical samples have improved by half to one order of magnitude (Figure 7), with more elements being added to routine commercial multielement packages (Caughlin, 2007 – this volume). Most exploration geochemical datasets now contain determinations on >40 elements, prompting further consideration of the support to target definition provided by previously difficult-to-analyse elements such as Re and Te.

### Selective Extractions

In response to new models that account for the development of weak dispersion haloes in transported cover and the routine availability of ICP methods, there have been significant advances in the use of selective extractions to isolate geochemical signals associated with specific mineral components or element forms in regolith. These are designed to physically separate the (low concentrations of) trace elements contributed to overburden by these secondary mechanisms, and associated with transient mineral phases in the regolith, from the trace element contents inherited from the transported regolith itself. A number of case studies are presented in Hall and Bonham-Carter (2002). In comparing the results of studies from a range of geochemical terrains (Yeager et al., 1998; Gray et al., 1998; Cohen et al., 1998) it would appear that selective extraction have met with more limited success in deeply weathered and arid terrains

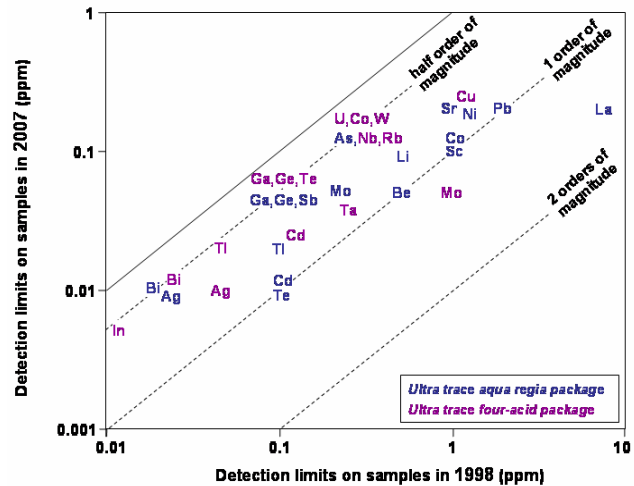


Figure 7: Typical improvements to detection limits for ultra trace ICP-MS/ICP-AES analytical packages based on aqua regia or 4-acid digestion of regolith, reported by commercial analytical companies.

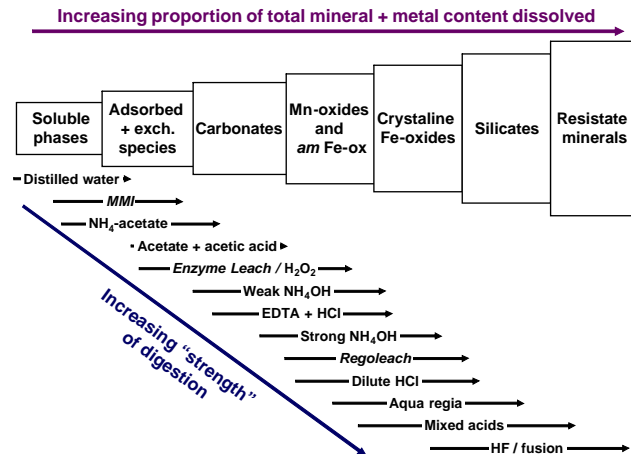
than in terrains such as the recently glaciated areas of the northern hemisphere.

Although by no means a new concept (the use of dilute HCl and similar selective extractant on soils and stream sediments dates from the 1950s) the development and application of selective extractions has tended to dominate analytical methods developments in geochemical exploration over the last decade. A general relationship between some common extractions and the mineral components they theoretically attack is presented in Figure 8. Whereas most studies have tended to be empirical investigations of the selective extraction response of regolith components to deeply buried underlying mineralisation, there has been limited work on the actual mechanisms of the extractions or the mineralogical-digestion response relationship (Cave et al., 2004; Dalrymple *et al.*, 2005; MacFarlane et al., 2005). Various commercial extraction methods have been developed with secret ingredients, but the more explicit methods typically contain various combinations of acids, chelants, reductants and exchangeable ions.

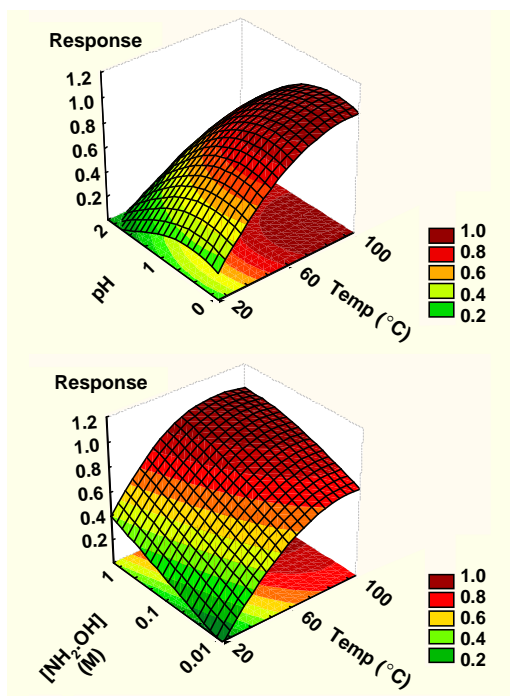
One feature common to selective extraction data, though usually more evident in the less vigorous digestions, is the high degree of spatial variability over small distances (Seneshen 1997; Gray et al., 1999; Rutherford 2002). While this phenomena was initially attributed to problems in controlling reaction conditions and the effects of small variations in sample mineralogy on digestion performance (e.g. carbonate altering reaction pH or Fe oxides causing re-precipitation of elements in the digestion), it is more likely that such variation over short distances (metre-scale) simply reflect the distribution of the migration paths (fractures and other discontinuities in the regolith) within which elements may concentrate, producing discrete anomalies within surface transported regolith until subsequent processes laterally redistribute those transported elements. Conversely, one effect of buried mineralisation may be to take a relatively uniform initial element distribution in transported regolith cover and induce “geochemical mottling” through the various processes described above (i.e. an increase



in spatial variance within the regolith without altering the bulk composition of the block of regolith overlying the mineralisation). Rather than obscuring the geochemical response to mineralisation, this high spatial variability may be the signal we need to detect.



**Figure 8:** Relationship between various selective geochemical extractions and regolith mineral components attacked.



**Figure 9:** Effects of pH versus temperature and reagent concentration versus temperature for the extraction of Mn from a soil by hydroxylamine.HCl, showing pH and temperature to be the most significant factors (from Dalrymple, 2007)

The development of field-based analytical devices has made some progress in the areas of field-portable XRF (Glanzman and Closs, 2007) although proper understanding of the limitations of

such methods is essential. The other area is in mineral analysis by portable spectral analytical devices, which can provide a rapid and detailed mineralogical characterisation of samples, which may itself provide indicators of mineralisation or alteration, and provide a more solid basis for subsequent interpretation of geochemical data (Taylor, 2000; Mauger et al., 2004).

## Quality Control

The need for quality control in geochemical exploration, from sampling to chemical analysis, remains critical in exploration geochemistry. Systematic QC protocols are especially critical for selective extractions as minor changes in extraction conditions can have severe effects on the extraction rates (Figure 9; Dalrymple, 2007). In relation to compilations of existing dataset, significant problems exist in stitching together different geochemical data sets, or leveling data derived from different regolith materials, especially where the metadata and quality control information are scarce (Agnew, 2004).

## DATA ANALYSIS

### Pattern Recognition and Anomaly Detection

A dichotomy continues to exist between stochastic modelling of geochemical data (exemplified by techniques such as factor analysis or fractal analysis) and deterministic modelling of geochemical data (exemplified by Pearce Element Ratio methods; Madeisky and Stanley, 1993).

The traditional approach to the interpretation of exploration geochemical data has been to define a “background” population based on some *a posteriori* distance metric relating observations to the centre of the dataset, or the *a priori* characteristics of samples collected distal to known mineralisation. Geochemical boundaries are subsequently set, beyond which observations are considered “anomalous” (either high or low), or data may simply be clustered with the assumption that the common or more highly populated groups are related to regional-scale or “environmental” geological processes and the samples affected by mineralisation will occur in small clusters or as extreme values (Cheng et al., 1996). Element associations still generally determined either by parametric clustering methods or various forms of principal components or factor analysis (Reimann et al., 2002), including spatial factor methods (Bailey and Krzanowski, 2000).

A number of inherent problems have been identified in such an approach, especially for large areas where geology, regolith, and landscape vary substantially (Reimann and Garrett, 2005) as they fail to recognise that background varies on all scales (Reimann and Caritat, 1998), from continents down to individual minerals.

Recent experience with selective geochemical data would suggest that the old notions of “background” and “anomalous” be abandoned in favour of recognising that the multifaceted geochemical characteristics of a suite of samples, reflecting the

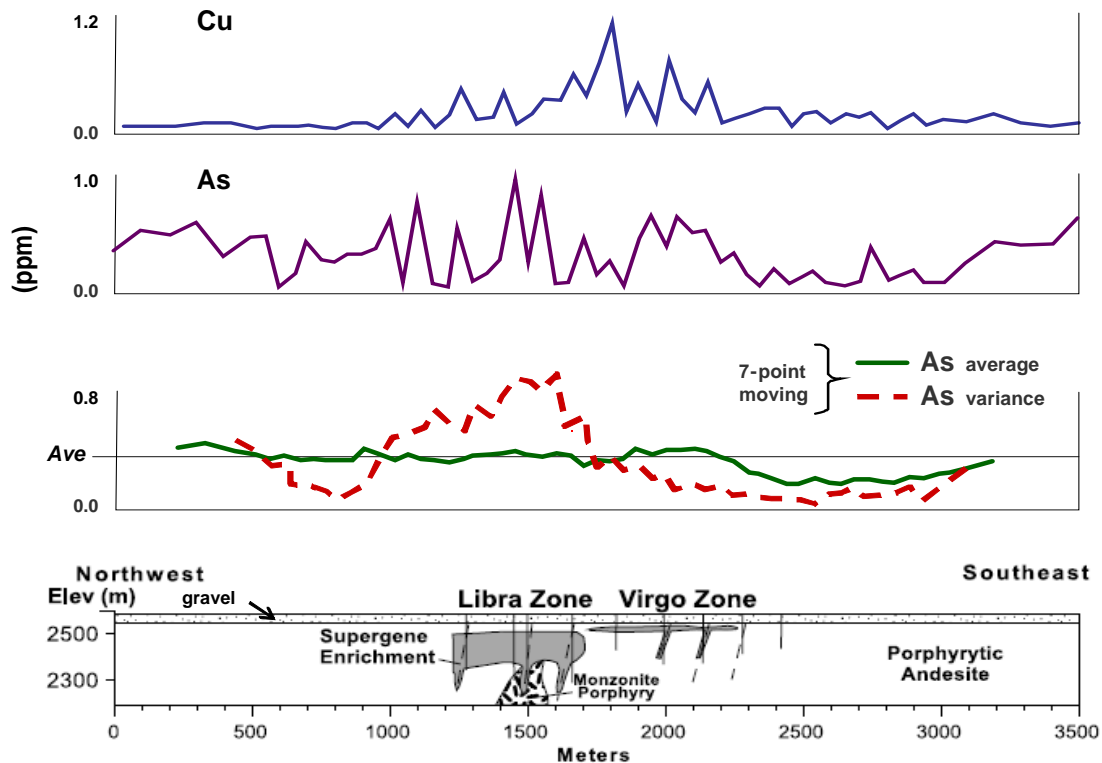
influence of a large number of complex interacting processes (ancient and modern). Instead, the objective of data processing should be to define that component of the total geochemical process variability that is associated with the influence of mineralisation, and establish the spatial relationship between mineralisation and samples in which that signal is present. It may be that the samples displaying the geochemical or mineralogical effects of mineralisation lie within the main cluster of observations rather than as outliers. The mineralised signal may just be just denser sub-clusters of points within a larger and more dispersed cluster of observations. Gauss is out and chaos is in.

An example of a new paradigm in geochemical signal detection, is drawn from the Enzyme Leach extraction element patterns for surface regolith samples collected over the Chimborazo deposit where mineralisation is covered by a thick gravel unit (Figure 10; Kelley et al., 2003). Elevated, but highly variable, Cu values form a continuous zone across mineralisation. Despite the appearance of “anomalies” in the As data, the application of a seven-point moving average across the profile indicates no addition of As to the gravels above mineralisation (i.e. all the As was probably inherited with the gravel itself). Conversely, a seven-point moving variance for the As data indicates significant increase in variance over mineralisation. Hence, the “signal” is a change in spatial

variance (in the As inherited with the gravels) rather than addition or depletion of that element.

Whereas the detection of population outliers or atypical values by classical means is still an important step in initial exploratory data analysis (Grunsky, 2007), most practitioners still focus on univariate rather than multivariate methods (Filzmoser et al., 2005). This probably reflects a lack of good grounding in mathematical theory and methods, the limitations of standard software packages when arrayed against the complexity of geochemical data, and the limited time allocated for company staff to properly analyse their geochemical datasets.

Isolating complex patterns of correlation between variables, associations among samples and the identification of mineralisation-induced effects in data through conventional multivariate parametric statistical procedures, may be biased or obscured by the presence of multivariate outliers and non-normal variable distributions (Reimann et al., 2002). Such procedures generally require substantial pre-processing of data prior to modeling and the recognition that geochemical variables display distributions that are complex and difficult to transform (Reimann and Filzmoser, 2002; Pison et al., 2003). Neural networks and the derivative self-organising maps are an alternate approach to revealing complex relationships



**Figure 10:** Comparison of Enzyme Leach Cu and As, and a seven-point moving average and moving variance for As, from a traverse over buried mineralisation at Chimborazo, Chile (data from Kelley et al., 2003).

within multivariate data sets and identifying anomalies, which are less dependent on the characteristics of the input data than conventional methods (Kohonen, 1995; Foody, 1997; Lalor and Zhang, 2001; Clare and Cohen, 2002). Other matrix decomposition methods have been considered, including semi-discrete decomposition (Skillicorn and Cohen, 2004).

One area of statistical analysis that has received significant attention has been the use of various forms of fractal and related analysis to separate univariate or multivariate populations (Cheng et al., 1994; Cheng and Agterberg, 1996; Sim et al., 1999; Gonçalves, 2001; Shen and Cohen, 2004; Li et al., 2004). Incorporation of the de Wijs model of element redistribution has also been incorporated (Xie and Bao, 2004; Agterberg, 2007). Variation in the fractal dimension of some geochemical patterns represents changes in the processes or factors controlling the geochemical values, for which one change (relating to one dimension) may be the introduction of the effects of mineralisation.

Ultimately the efficiency of a geochemical exploration program will be defined by the percentage of errors in the categorisation of samples into the set whose geochemistry (and mineralogy) reflects the effects of mineralisation and the set that does not. The data analysis component of this task may require the provision of substantial resources in technical staff and time.

#### Data Integration and Spatial Analysis

Over the last decade the increase in performance of personal computers and availability of a range of user-friendly software packages permit easier handling of large datasets in spatial frameworks (GIS) and advanced iterative manipulation linked to more flexible data visualisation options (Aaron and Brown, 2004; Racic, 2006). An example is the integration of multivariate geochemical data, PCA and topography has been shown for Sumatra (Grusnick and Smee, 2002).

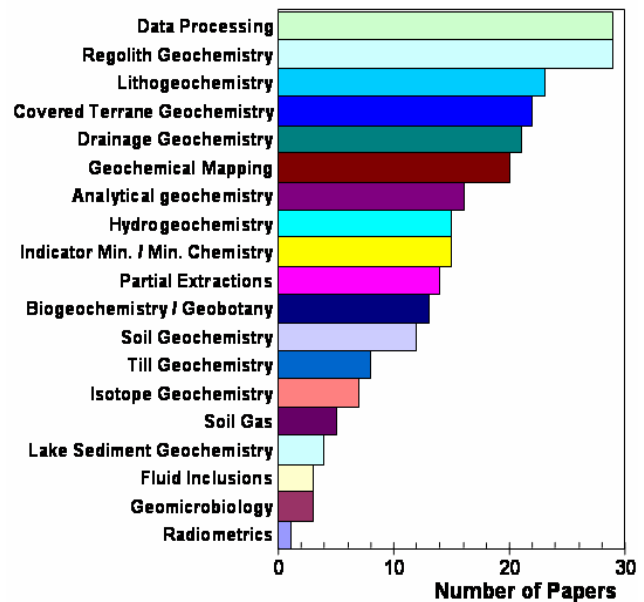
### CONCLUSIONS

#### Key Advances in Exploration Geochemistry Over the Decade – Did We Progress?

The decade has been marked by a series of small to medium steps in the development of exploration geochemical theory and practice. While the promise of selective geochemical extractions as the “silver bullet” for areas with thick transported or deeply weathered cover has not materialised, it has prompted research into the fundamental processes of geochemical dispersion and new approaches to the definition and the detection of geochemical patterns that might be related to the effects of underlying mineralisation. With new models there is opportunity to mine old datasets (Stegman, 2002; Agnew, 2004). The generation of a series of high quality, regional to sub-continental scale geochemical and regolith maps, has rekindled general interest in landscape geochemistry and demonstrated that geology is usually the main determinant of regolith geochemistry.

These features can be seen in the distribution of papers in the three principal journals in which exploration geochemical research tends to be published (Figure 11). Whereas data processing is the surprise winner, selective extractions is probably the underlying area of research focus if the papers designated as being mainly analytical, exploration in covered terrains and partial extractions are examined.

A major discovery might be that the best tool for detecting deeply buried sulphide mineralisation is the simple pH meter (Smee, 2003).



Applied Geochemistry (n=24)

Geochemistry: Exploration, Environment & Analysis (n=116)

Journal of Geochemical Exploration (n=120)

Figure 11: Distribution of “exploration geochemistry” papers published in GEEA, JGE and AG, 1997-2007, allocated to main subject areas.

#### Current Challenges to Metals Exploration – New Commodities, New Terrains, No Workers

The detection of mineralisation in areas dominated by transported regolith cover remains the principal challenge for exploration geochemistry, with U now added to the list of commodities for which immediate future demand seems set to rise. Continuing interaction between exploration geochemistry and environmental geochemical practitioners is certain – it is common for both groups to be asking the same fundamental questions about the factors controlling the behaviour of metals in the surficial environment (Plumlee and Logsdon, 1997). Such convergence has been recognised in renaming of the Association of Exploration Geochemists into the Association of Applied Geochemists in 2004, and moves to provide opportunities (publications and conferences) where both sides of the artificial geochemical divide can meet.

The most serious challenge is not technical. The upturn in commodities has been met by increasing severity in the shortage of suitably qualified and experienced scientists, especially exploration geochemists and geophysicists, coupled to a progressive contraction of geology in the university sector (Cohen, 2004). This will have further critical implications for the future research support provided to industry (Hogan, 2004).

As governments now view education as another commodity, the laws of supply and demand need to be carefully considered by industry and ways in which the decline in the number of universities able to deliver credible geoscience programs capable of providing the initial training and career gateway into the exploration and mining industry can be reversed. It is a cold fact; no staff, no graduates / no graduates, no exploration.

### Future Research Direction – Grasping the Nettle

Our geochemical crystal ball suggests a number of future research directions that will be supported by further developments and improvements in analytical methods and the assembly of multi-disciplinary research teams. A number of these are further considered by Coker (2007, this volume). The mechanisms of element dispersion must be extending by more detailed investigations of the role of biological systems in element mobilisation and precipitation (the presence of specific gene sequences may become another variable to measure in regolith samples).

Broad-based isotopes analysis, from the light to the heavy elements, will become more routine. This will be supported by increased research efforts to establish the regolith isotopic signatures characteristic of different mineral deposits under various regolith setting and geological terrains.

We will abandon the concept of fixed geochemical “baselines”, “backgrounds” and “anomalies”, in favour of recognizing geochemical signals relating to the effects of mineralisation, especially in multivariate data, and focusing on suitable methods to isolating those processes that have affected the geochemistry of our samples and which are of interest to explorers. Anomaly detection will migrate from the algorithmic to the heuristic, from the parametric to more robust and knowledge-based approaches.

There will be continued integration between the exploration and environmental geochemical disciplines, in recognition that deposits cannot be mined until:

- (i) they are discovered and
- (ii) proper environmental controls on mining can be maintained.

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(Lakewood). A brief overview such as this will inevitably fail to acknowledge many of the significant steps that have been taken by geochemists in the development of geochemical exploration theory and practice, and we apologise to those individuals in advance. With the passing of Professor John Webb, the first generation of exploration geochemical gurus (the primary anomalies) is now almost at an end and the subsequent generation (the secondary anomalies) acknowledge the strong foundations upon which the discipline continues to grow.

### REFERENCES

- Aaron, D. and Brown, D.A., 2004, Production of geochemical atlas pages using Datadesk and ArcGIS, in I.C. Roach, ed, *Regolith 2004: CRC LEME*, 32-36.
- Agnew, P.D., 2004, Applications of geochemistry in targeting with emphasis on large stream and lake sediment data compilations, in *Predictive Mineral Discovery Under Cover: Society of Economic Geology Symposium*, 27 Sept–1 Oct, Perth.
- Agterberg, F., 2007, New applications of the models of de Wijs in regional geochemistry: *Mathematical Geology*, 39, 1–25.
- Anand, R.R. and de Broekert, P., eds, 2005, *Regolith-landscape Evolution Across Australia: CRC LEME*.
- Anand, R.R. and Paine, M., 2002, Regolith geology of the Yilgarn Craton, Western Australia - Implications for exploration: *Australian Journal of Earth Sciences*, 49, 4-162.
- Anand, R.R., 2000, Regolith and geochemical synthesis of the Yandal greenstone belt, in G.N. Phillips and R.R. Anand, eds, *Yandal Greenstone Belt, Regolith, Geology and Mineralisation: Australian Institute of Geoscientists Bulletin*, 31, 79-112.
- Anand, R.R., Cornelius, M. and Phang, C., 2007, Use of vegetation and soil in mineral exploration in areas of transported overburden, Yilgarn Craton, Western Australia - A contribution towards understanding metal transportation processes: *Geochemistry: Exploration, Environment, Analysis* (in press).
- Antropova, L.V., Goldberg, I.S., Voroshilov, N.A. and Ryss, J.S., 1992, New methods of exploration for blind mineralization in the USSR: *Journal of Geochemical Exploration*, 43, 157–166.
- Arne, D.C., Stott, J.E. and Waldron, H.M, 1999, Biogeochemistry of the Ballarat East goldfields, Victoria, Australia: *Journal of Geochemical Exploration*, 67, 1–14.
- Bailey, T.C. and Krzanowski, W.J., 2000, extensions to spatial factor methods with an illustration in geochemistry: *Mathematical Geology*, 32, 657–682.
- Bamba, O., Parisot, J.C., Grandin, G. and Beauvais, A., 2002, Ferricrete genesis and supergene behaviour in Burkina Faso, West Africa: *Geochemistry, Exploration, Environment, Analysis*, 2, 15-25.
- Blight, D.F., 2002, Observations on the funding of geological survey organizations: *Proceedings of the 2nd World Mining Ministers Forum*, 13–15 March, Toronto.
- Bolster, J.S.M., 1999, Regolith mapping: is it necessary? *Exploration Geochemistry for the New Millennium: Australian Institute of Geoscientists Bulletin*, 30, 125-135.

- Bølviken, B. and Logn, O., 1975, An electrochemical model for element distribution around sulphide bodies, in I. Elliott and K. Fletcher, eds., *Geochemical Exploration 1974*: Elsevier, 631–648.
- Bowler, J., 2002, Ministerial inquiry into greenfields exploration in Western Australia and Government response to the inquiry: Western Australian Government.
- Brown, A.D., 2004, Regolith-landform maps are an essential tool for interpreting regolith geochemistry - the white dam, SA, experience, in S.M. Hill, ed, *Proceedings of the CRC LEME Regional Regolith Symposia 2004*: CRC LEME.
- Butt, C.R.M., Lintern, M.J. and Anand, R.R., 2000, Evolution of regolith and landscapes in deeply weathered terrain-implications for geochemical exploration: *Ore Geology Reviews*, 16, 167-183.
- Butt, C.R.M., Robertson, I.D.M., Scott, K.M. and Cornelius, M., eds, 2005. *Regolith expression of Australian ore systems*: CRC LEME.
- Cairns, C.J., McQueen, K.G. and Leah, P.A., 2001, Mineralogical controls on element dispersion in regolith over two mineralised shear zones near the Peak, Cobar, NSW: *Journal of Geochemical Exploration*, 72, 1–21.
- Cairns, C.J., McQueen, K.G. and Leah, P.A., 2001, Mineralogical controls on element dispersion in regolith over two mineralised shear zones near the Peak, Cobar, NSW: *Journal of Geochemical Exploration*, 72, 1–21.
- Cameron, E.M. and Leybourne, M.I., 2005, Relationship between ground water chemistry and soil geochemical anomalies at the Spence copper porphyry deposit, Chile: *Geochemistry: Exploration, Environment, Analysis*, 5, 135–145.
- Cameron, E.M. and Leybourne, M.I., 2006, Atacamite in the oxide zone of copper deposits in northern Chile - Involvement of deep formation waters?: *Mineralium Deposita*, 42, 205–218.
- Cameron, E.M., Hamilton, S.M., Leybourne, M.I., Hall, G.E.M. and McClenaghan, M.B., 2004, Finding deeply buried deposits using geochemistry: *Geochemistry: Exploration, Environment, Analysis*, 4, 7–32.
- Cameron, E.M., Leybourne, M.I. and Kelley, D.L., 2002, Exploring for deeply-covered mineral deposits: Formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized ground waters: *Geology*, 30, 1007–1010.
- Cameron, E.M., Leybourne, M.I. and Kelley, D.L., 2005, Exploring for deposits under deep cover using geochemistry: *Society of Economic Geology Newsletter*, 63, 5–15.
- Cauglin, B., 2007 (this volume), *Developments in Analytical Technology*: *Proceedings of Exploration 07*.
- Cave M.R., Milodowski A.E. and Friel, E.N., 2004, Evaluation of a method for identification of host physico-chemical phases for trace metals and measurement of their solid-phase partitioning in soil samples by nitric acid extraction and chemometric mixture resolution: *Geochemistry: Exploration, Environment, Analysis*, 4, 71-86.
- Cheng, Q. and Agterberg, F.P., 1996, Multifractal modelling and spatial statistics: *Mathematical Geology*, 28, 1–16.
- Cheng, Q., Agterberg, F.P. and Ballantyne, S.B., 1994, Separation of geochemical anomaly from background by fractal methods: *Journal of Geochemical Exploration*, 51, 109–130.
- Cheng, Q., Agterberg, F.P. and Bonham-Carter, G.F., 1996, A spatial analysis method for geochemical anomaly separation: *Journal of Geochemical Exploration*, 56, 183–195.
- Clare A.P. and Cohen D.R., 2002, A comparison of unsupervised neural networks and k-means clustering in the analysis of multi-element stream sediment data: *Geochemistry: Exploration, Environment, Analysis*, 1, 119–134.
- Closs, L.G., 1997, *Exploration Geochemistry: Expanding Contributions to Mineral Resource Development*, in A.G. Gubins, ed, *Proceedings of Exploration 97, Fourth Decennial International Conference on Mineral Exploration*: paper 1, 3–8.
- Cohen, D.R., 2004, Who will deliver the last classical exploration geochemistry course?: *Explore*, 123, 1-.
- Cohen, D.R., Shen, X.C., Dunlop, A.C. and Rutherford, N.F., 1998, A comparison of selective extraction soil geochemistry and biogeochemistry in the Cobar Area, NSW: *Journal of Geochemical Exploration*, 61, 173–190.
- Coker, W.B. and DiLabio, R.N.W., 1989, Geochemical exploration in glaciated terrain: geochemical responses, in G.D. Garland, ed, *Proceedings of Exploration '87*: Ontario Geological Survey, Special Volume, 3, 336–383.
- Coker, W.B., 2007 (this volume), *Future research directions in exploration geochemistry*: *Proceedings of Exploration 07*.
- Cornelius, M., Morris, P.A. and Cornelius, A.J., 2006, *Laterite geochemical database for the southwest Yilgarn Craton, Western Australia*: CRC LEME Open File Report 201 and CSIRO Report P2006/75.
- Dalrymple, I.J., 2007, *An approach to the optimisation of partial extractions for geochemical exploration*: PhD thesis, University of New South Wales.
- Dalrymple, I.J., Cohen, D.R. and Gatehouse, S.G., 2005, Optimization of partial extraction chemistry for buffered acetate and hydroxylamine leaches: *Geochemistry: Exploration, Environment, Analysis*, 5, 279-285.
- Darnley, A.G., Björklund, A., Bølviken, B., Gustavsson, N., Koval, P.V., Plant, J.A., Steinfeld, A., Tauchid, M., Xuejing, X., Garrett, R.G. and Hall, G.E.M., 1995, *A global geochemical database for environmental and resource management: Recommendations for international geochemical mapping*: Final Report of IGCP Project 259. UNESCO Publishing.
- Davissou, M.L., Presser, T.S. and Criss, R.E., 1994, *Geochemistry of tectonically expelled fluids from the northern Coast ranges, Rumsey Hills, California, USA*: *Geochimica et Cosmochimica Acta*, 58, 1687–1699.
- Dunn, C.E., 2007 (this volume), *New Perspectives on Biogeochemical Exploration*: *Proceedings of Exploration 07*.
- Dunn, C.E., 2007, *Biogeochemistry in Mineral Exploration: Handbook of Exploration and Environmental Geochemistry*, volume 9: Elsevier.
- Filzmoser, P., Garrett, R.G. and Reimann, C., 2005, Multivariate outlier detection in exploration geochemistry: *Computers and Geosciences*, 31, 579–587.
- Foody, G.M., 1997, Fully fuzzy supervised classification of land cover from remotely sensed imagery with an artificial neural network: *Neural Computing and Applications*, 5, 238–247.
- Friske, P.W.B., 1997, Putting it all together—Surficial geochemistry maps for large areas of Canada, in A.G. Gubins, ed, *Proceedings*

- of Exploration 97, Fourth Decennial International Conference on Mineral Exploration: paper 45, 363–364.
- Giblin, A. and Mazzuchelli, R., 1997, Groundwater geochemistry in exploration: an investigation in the Black Flag district, Western Australia: *Australian Journal of Earth Sciences*, 44, 433–443.
- Glanzman, R.K. and Closs, L.G., 2007 (this volume), Field portable XRF geochemical analysis – Its contribution to in situ, real-time project evaluation: *Proceedings of Exploration 07*.
- Goldberg, I.S., 1998, Vertical migration of elements from mineral deposits: *Journal of Geochemical Exploration*, 61, 191–202.
- Gonçalves, M.A., 2001, Characterization of geochemical distributions using multifractal models: *Mathematical Geology*, 33, 41–61.
- Govett, G.J.S., 1973, Differential secondary dispersion in transported soils and post-mineralization rocks: An electrochemical interpretation, in M.J. Jones, ed, *Geochemical Exploration 1972*: Institute of Mining and Metallurgy, 81–91.
- Gray, D.J., Wildman, J.E. and Longman G.D., 1999, Selective and partial extraction analyses of transported overburden for gold exploration in the Yilgarn Craton, Western Australia: *Journal of Geochemical Exploration*, 67, 51–66.
- Grunsky, E.C. and Smee, B.W., 2002, The differentiation of soil types and mineralization from multi-element geochemistry using multivariate methods and digital topography: *Journal of Geochemical Exploration*, 67, 287–299.
- Grunsky, E.C., 2007 (this volume), Evaluating and Interpreting Regional Geochemical Survey Data: *Proceedings of Exploration 07*.
- Gustavsson N, Bølviken B, Smith DB and Severson RC. 2001, Geochemical landscapes of the conterminous United States—new map presentations for 22 elements: U.S. Geological Survey Professional Paper, 1648.
- Hall, G.E.M. and Bonham-Carter, G.F., 1998, Selective extractions: *Journal of Geochemical Exploration*, 61.
- Hall, G.E.M., Hamilton, S.M., McClenaghan, M.B. and Cameron, E.M., 2004, Secondary geochemical signatures in glaciated terrain, in *Predictive Mineral Discovery Under Cover*: Society of Economic Geology symposium, 27 Sept–1 Oct, Perth.
- Hamilton, S.M., 1998, Electrochemical mass-transport in overburden: a new model to account for the formation of selective-leach geochemical anomalies in glacial terrain: *Journal of Geochemical Exploration*, 63, 155–172.
- Hamilton, S.M., 2000, Spontaneous potentials and electrochemical cells, in geochemical remote sensing of the sub-surface, in M. Hale and G.J.S. Govett, eds, *Handbook of Exploration Geochemistry volume 7*: Elsevier, 81–119.
- Hamilton, S.M., Cameron, E.M., McClenaghan, M.B. and Hall, G.E.M., 2004a, Redox, pH and SP variation over mineralization in thick glacial overburden, Part I: Methodologies and field investigation at the Marsh zone gold property: *Geochemistry: Exploration, Environment, Analysis*, 4, 33–44.
- Hamilton, S.M., Cameron, E.M., McClenaghan, M.B. and Hall, G.E.M., 2004b, Redox, pH and SP variation over mineralization in thick glacial overburden, Part II: field investigation at Cross lake VMS property: *Geochemistry: Exploration, Environment, Analysis*, 4, 45–58.
- Hamilton, S.M., Hall, G.E.M., McClenaghan, M.B., Cameron, E.M., 2003, Rapid mass-transport of elements through clay and the possible role of redox gradients: *Proceedings of the 6th International Symposium on Environmental Geochemistry*, September 8, Edinburgh.
- Harley, S.L. and Kelly, N.M., 2007, Zircon tiny but timely: *Elements*, 3, 3–18.
- Highsmith, P., 2004, Overview of soilgas theory: *Explore*, 122, 1-.
- Hogan, L., 2004, Research and development in exploration and mining - Implications for Australia's gold industry: Australian Bureau for Agricultural and Resource Economics, e-Report 04.3.
- Kelley, D.L., Hall, G.E.M., Closs, L.G., Hamilton, I.C. and McEwen, R.M., 2003, The use of partial extraction geochemistry for copper exploration in northern Chile: *Geochemistry: Exploration, Environment, Analysis*, 3, 85–104.
- Kirste, D., de Caritat, P. and Dann, R., 2003, The application of the stable isotopes of sulfur and oxygen in groundwater sulfate to mineral exploration in the Broken Hill region of Australia: *Journal of Geochemical Exploration*, 78/79, 81–84.
- Kohonen, T., 1995. *Self-Organizing Maps*: Springer-Verlag.
- Lalor, G.C. and Zhang, C., 2001, Multivariate outlier detection and remediation in geochemical databases: *The Science of the Total Environment*, 281, 99–109.
- Lane, R., Green, A., Golding, C., Owers, M., Pik, P., Plunkett, C., Sattel, D. and Thorn, B., 2000, An example of 3D conductivity mapping using the TEMPEST airborne electromagnetic system: *Exploration Geophysics*, 31, 162–172.
- Lawrance, L.M., 1999, Multi-element dispersion in Mesozoic basin sediment over the Osborne deposit, northern Queensland - implications for regional geochemical exploration in buried terrain, in *Exploration Under Cover*: Australian Institute of Geoscientists Bulletin, 28, 73–81.
- Li, C., Ma, T. and Cheng, J., 2004, A fractal interpolatory approach to geochemical exploration data processing: *Mathematical Geology*, 36, 593–606.
- Li, J. and Wu, G. (Chief compilers). 1999, *Atlas of the Ecological Environmental Geochemistry of China*: Geological Publishing House.
- Lintern, M.J., 2005, Biogeochemical anomalies at barns gold prospect (Eyre Peninsula, South Australia), in I.C. Roach, ed, *Regolith 2005 – Ten Years of CRC LEME*: CRC LEME, 195–196.
- Macdonald, J., 2002, Obtaining leverage through geoscience: Options for governments and mining companies: *Proceedings of the 2nd World Mining Ministers Forum*, 13–15 March, Toronto.
- MacFarlane, W.R., Kyser, T.K., Chipley, D., Beauchemin, D. and Oates, C., 2005, Continuous leach inductively coupled plasma mass spectrometry: applications for exploration and environmental geochemistry: *Geochemistry: Exploration, Environment, Analysis*, 5, 123–134.
- Madeisky, H.E. and Stanley, C.R., 1993, Lithochemical exploration for metasomatic zones associated with volcanic-hosted massive sulphide deposits using Pearce Element Ratio analysis: *International Geological Reviews*, 35, 1121–1148.
- Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B. and Perdrix, J.L., 1998, Application of the mobile metal ion technique in geochemical exploration: *Journal of Geochemical Exploration*, 61, 87–102.
- Mauger, A.J., Keeling, J.L. and Huntington J.F., 2004, Bring Remote Sensing Down To Earth: CSIRO Hylogger as applied to the

- Tarcoola Goldfield, South Australia, in Proceedings of the 12th Australasian Remote Sensing and Photogrammetry Conference, Freemantle, 18-22 October, 2004.
- McGrath, S.P. and Loveland, P.J., 1992, The soil geochemical atlas of England and Wales: Blackie Academic and Professional.
- Muir-Wood, R., 1994, Earthquakes, strain-cycling and the mobilization of fluids, in J. Parnell, ed, Geofluids: origin, migration and evolution of fluids in sedimentary basins, Special Publication: Geological Society of London, 78, 85–98.
- Nur, A., 1974, Matsushiro, Japan, earthquake swarm: confirmation of dilatancy-fluid diffusion model: *Geology*, 2, 217–221.
- O'Reilly, S.Y., Griffin, W.L. and Belousova, E.A., 2004, TerraneChron - delivering a competitive edge in exploration, in Predictive Mineral Discovery Under Cover: Society of Economic Geology symposium, 27 Sept–1 Oct, Perth.
- Pain, C.F., Chan, R.A., Craig, M.A., Gibson, D.L., Kilgour, P. and Wilford, J.R., 2001, RTMAP Database Field Book and Users Guide: CRC LEME, Report 13, Perth.
- Pillans, B., 2005, Geochronology of the Australian regolith, in R.R. Anand and P. de Broekert, eds, Regolith landscape Evolution across Australia: CRC LEME, 41-52.
- Pirlo M.C. and Giblin A.M., 2004, Application of groundwater-mineral equilibrium calculations to geochemical exploration for sediment-hosted uranium: observations from the Frome Embayment, South Australia, *Geochemistry: Exploration, Environment: Analysis*, 4, 113-127.
- Pison, G., Rousseeuw, P.J., Filzmoser, P. and Croux, C., 2003, Robust factor analysis: *Journal of Multivariate Analysis*, 84, 145–172.
- Plant JA, Smith D, Smith B and Williams L, 2000, Environmental geochemistry at the global scale: *Journal of the Geological Society*, 157, 837–849.
- Plant, J.A., Reeder, S., Salminen, R., Smith, D.B., Tarvainen, T., De Vivo, B. and Petterson, M, G. 2003, The distribution of uranium over Europe: geological and environmental significance: *Applied Earth Science*, 112, 221–238.
- Plumlee, G.S. and Logsdon, M.H., eds., 1997, The environmental geochemistry of mineral deposits: *Reviews in Economic Geology*, 6, Society of Economic Geologists.
- Polito P.A., Clarke J.D.A., Bone Y. and Viellenave J., 2002, A CO<sub>2</sub>-O<sub>2</sub>-light hydrocarbon-soil-gas anomaly above the Junction orogenic gold deposit: a potential, alternative exploration technique: *Geochemistry, Exploration, Environment, Analysis*, 2, 333-344.
- Racic, L., 2006, Extending the limits of earth data visualization and exploration: *First Break*, (European Association of Geoscientists and Engineers), 24, 61–65.
- Reimann C. and de Caritat P., 1998, Chemical elements in the environment - factsheets for the geochemist and environmental scientist: Springer-Verlag.
- Reimann, C. and Filzmoser, P., 2000, Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data: *Environmental Geology*, 39, 1001–1014.
- Reimann, C. and Garrett, R.G., 2005, Geochemical background–concept and reality: *Science of the Total Environment*, 350, 12–27
- Reimann, C., Filzmoser, P. and Garrett, R.G., 2002, Factor analysis applied to regional geochemical data: problems and possibilities: *Applied Geochemistry*, 17, 185–206.
- Rohrlach, B.D. and Loucks, R.R., 2005, Multi-million-year cyclic ramp-up of volatiles in a lower crustal magma reservoir trapped below the Tampakan copper-gold deposit by Mio-Pliocene crustal compression in the southern Philippines, in T.M. Porter, ed., Super porphyry copper and gold deposits: A global perspective: *PGC Publishing*, 2, 270.
- Rutherford, N.F., 2002, The regolith, background, anomalies and partial leaches: ALS–Chemex News 2001–1.
- Rutherford, N.F., Lawrance, I.M. and Sparks, G., 2005, Osborne copper-gold deposit, Cloncurry Mining District, north west Queensland, in *Regolith Expressions of Australian Ore Systems*: CRC LEME.
- Salminen, R. (ed) and 27 others, 1998, FOREGS Geochemical sampling Field Manual: Geological Survey of Finland Guide 47.
- Salminen, R. (ed) and 30 others, 2005, The Geochemical Atlas of Europe: Geological Survey of Finland.
- Sato, M. and Mooney, H.M., 1960, The electrochemical mechanism of sulphide self-potentials: *Geophysics*, 25, 226–249.
- Seneshen, D.M., 1997, The applicability of partial extractions to mineral exploration in areas of transported overburden: PhD thesis, Queens University, Kingston.
- Shen, W. and Cohen, D.R., 2005, Fractally invariant distributions and an application in geochemical exploration: *Mathematical Geology*, 37, 895–913.
- Sibson, R.H., 1981, Fluid flow accompanying faulting: Field evidence and models, in D.W. Simpson and P.G. Richards, eds, Earthquake prediction: An internal review, Maurice Ewing Series: American Geophysical Union, 4, 593–603.
- Sibson, R.H., 2001, Seismogenic framework for hydrothermal transport and ore deposition, in Structural controls on ore genesis, in J.P. Richards and R.M. Tosdal, eds, *Reviews in Economic Geology*: Society of Economic Geologists, 14, 25–50.
- Skillicorn, D.B. and Cohen, D.R., 2004, Detecting mineralisation using partial element extraction - A Case study, in 7th workshop on mining scientific and engineering datasets, 4th SIAM international conference on data mining, Florida, April 24, 2004.
- Smee, B.W., 1983, Laboratory and field evidence in support of the electrochemically-enhanced migration of ions through glaciolacustrine sediment: *Journal of Geochemical Exploration*, 19, 277–304
- Smee, B.W., 1998, A new theory to explain the formation of soil geochemical responses over deeply covered gold mineralization in arid environments: *Journal of Geochemical Exploration*, 61, 149–172.
- Smee, B.W., 2003, Theory behind the use of soil pH measurements as an inexpensive guide to buried mineralisation, with examples: *Explore*, 118, 1-.
- Stegman, C., 2002, Near mine exploration in the Cobar Goldfield – Making use of our greatest asset, in C. Torrey, ed, *Exploration in the Shadow of the Headframe – Getting a New Life on Lease*: SMEDG–AIG Symposium, Oct 11, 2002, Sydney
- Taylor, G.R., 2000, Mineral and Lithology Mapping of Drill Core Pulps using Visible and Infrared Spectrometry: *Natural Resources Research*, 9, 257-268.

- Tchalenko, J.S., 1973, The Kashmir (Turshiz) 1903 and Torbat-e Heidarieh 1923 earthquakes in Central Khorassan (Iran): *Annali di Geofisica*, 26, 29–40.
- Unruh, J.R., Davisson, M.L., Criss, R.E. and Moores, E.M., 1992, Implications of perennial saline springs for abnormally high fluid pressures and active thrusting in western California: *Geology*, 20, 431–434.
- US Geological Survey, 2004, The national geochemical survey – Database and documentation: US Geological Survey, Open File Report, 2004–1001.
- Volden, T., Reimann, C., Pavlov, V., Caritat, P. de and Äyräs, M., 1997, Overbank sediments from the surroundings of the Russian nickel mining and smelting industry on the Kola Peninsula: *Environmental Geology*, 32, 175–185.
- Wang X., Xie, X., Cheng, Z. and Liu, D., 1999, Delineation of regional geochemical anomalies penetrating through thick cover in concealed terrains – A case history from the Olympic Dam deposit, Australia: *Journal of Geochemical Exploration*, 66, 85–97.
- Xie, S. and Bao, Z., 2004, Fractal and multifractal properties of geochemical fields: *Mathematical Geology*, 36, 847–864.
- Xie, X. and Cheng, H., 1997, The suitability of floodplain sediment as a global sampling medium: Evidence from China: *Journal of Geochemical Exploration*, 58, 51–61.
- Xujing, X., Darwen, L., Yunchuan, X., Guangsheng, Y. and Changyun, L., 2004, Geochemical blocks for predicting large ore bodies – Concept and methodology: *Journal of Geochemical Exploration*, 82, 77–91.
- Yeager, J.R., Clark, J.R., Mitchell, W. and Renshaw, R., 1998, Enzyme Leach anomalies associated with deep Mississippi Valley-type zinc ore bodies at the Elmwood Mine, Tennessee: *Journal of Geochemical Exploration*, 61, 103–112.