Advances in Exploration Geochemistry, 2007 to 2017 and Beyond


INTRODUCTION

Geochemistry continues to be a major component of mineral exploration and evaluation programs on a global basis. Because of a series of economic crises over the past decade, which saw major exploration and mining companies reducing assets and staff, breakthrough research in exploration geochemistry has also declined as industry funds to finance collaborative research dried up. In addition, geochemical exploration has required less innovation as traditional techniques have continued to be used with success in shallowly covered or outcropping terrains. The industry reliance on past protocols and workflows has possibly slowed uptake of new technologies in geochemistry, although as exploration must extend into deeper cover or more challenging environments in many continents, a reliance on new developments in technology and knowledge is both required and inevitable.

EXPLORATION UNDERCOVER

The reliable and robust detection of mineral deposits under younger, often exotic overburden (cover), remains a challenge. Except for the AMIRA projects P778 and P778A (Anand et al., 2016), large scale coordinated research efforts have been absent over the past decade. In part this reflected both a frustration by industry at the lack of cohesive results and models which could be applied, coupled with a declining ability to raise significant research funding during various economic crises and downturns in the period 2007-2017, resulting in the fragmentation of research efforts. Towards the end of the decade, research was being revitalized despite the poor economic climate with initiatives such as the UNCOVER program (Noble and Christie 2015) in Australia and the Exploration Geochemistry Initiative at the University of British Columbia, Canada (Winterburn, 2016). The Deep Exploration Technologies Cooperative Research Centre (DET CRC) in Australia also led the development of technology applications through cover, although
the focus was on drilling with components related to geochemistry with in-line or near-real-time geochemistry applied to the drilling workflow (Fabris et al., 2015).

**Arid Regions**

Major arid regions with ongoing exploration programs include Australia, Chile, southern Peru, south-western USA and China. Cover materials range from thick alluvial and windblown deposits through to deep colluvium-filled basins that hide previously outcropping mineral deposits. Exploration through this often poorly cemented and poorly compacted material remains a challenge with exploration practices having changed little over the decade despite promising research results in the previous decade. Australia is the principle exception, where the work of Anand and others from the collaborative multi-industry AMIRA program has developed a series of process-driven models (Anand et al., 2016) constraining the formation of geochemical anomalies in the surface environment in the extensively weathered and buried terrains of Australia. In the model of Anand et al. (2014) and Anand et al. (2016), much of the surface geochemistry is presumed to be derived through recycling of the elements by the interaction of vegetation with ground water in contact with mineralization or paleo-water tables with anomalous metal accumulations (Figure 1). The models place constraints on the production of responses in that there must have been interaction between vegetation and the ground water or weathered saprolite, either currently or in the past, to generate a signal, and that the accumulation of the signal must exceed the rate of erosion or burial. Basin depth is considered a significant factor with the implication that basin depth, the depth of the current water table and knowledge of the presence of a paleo-water table become key decision points in assessing the viability of either soil chemistry or biogeochemistry within an area.

Research and application of exploration geochemical techniques to see through the transported gravels in northern Chile following on from the research of Cameron et al. (2004) and others appear relatively limited with only a small number of companies having taken the research results into practical applications. Results from the Chilean phase of the AMIRA P778 project indicate limited success at identifying the presence of the Inca de Oro porphyry through transported cover (Soto, 2010; Luca, 2012; Lopez, 2014). Research, however, demonstrated yet again, the movement of metals into ground water (Leybourne and Cameron, 2008; Soto 2010), movement of ground water to the surface through fractures (Leybourne et al., 2013) and furthermore the significant positive fractionation of the copper isotope signature from the mineralization (Figure 2) in the ground water compared to the original ore. Where ground water is in contact with chalcocite in leachcaps, the fractionation is even more pronounced as the chalcocite, having been precipitated following lixiviation is already positively enriched. (Mathur et al., 2014).

![Figure 1: Potential mechanisms for the generation of geochemical responses in weathered transported regolith in Australia. Access of vegetation to palaeo-accumulations or the current water table in contact with mineralization are considered key factors in the formation of geochemical responses at the surface (Anand et al., 2016).](image1)

![Figure 2: Copper isotope ratios of ores (black) and associated groundwaters (light grey) for selected deposits (Mathur et al., 2014).](image2)
Recent Glacial

Indicator minerals abundance and chemistry continues to be a dominant technique for mineral exploration in regions of recent glacial retreat. Detailed mineral indicator studies around a series of porphyry deposits in central British Columbia (Plouffe et al., 2016) further demonstrate both the value of detailed indicator mineral studies, as well as the link between indicator minerals and clay trace element chemistry. Applying the results of various mineral chemistry studies (e.g., Bouzari et al., 2016; Cooke et al., 2014) has allowed the expansion of indicator mineral studies from simple grain counts to mineral chemistry studies more akin to kimberlite exploration. Whilst geochemical proximity indicators become invalid, given the transportation of the material, fertility indicators still add substantial value.

Figure 3: Cathodoluminescence images of apatites from altered host rocks. (a) Mount Polley apatite occurring with K feldspar + magnetite alteration, showing that green-luminescent apatite has overgrown and locally replaced brown-luminescent apatite, (b) Apatite grain occurring with K silicate alteration overprinted by phyllic alteration, showing an early bright green-luminescent apatite cut by dull grey-luminescent apatite (Bouzari et al., 2016).

Whilst several recent studies aimed at direct “vertical” detection through till (e.g., Heberlein, 2010; Bissig et al., 2013; Heberlein et al., 2013) have evaluated various soil horizons in conjunction with multiple digests, these studies generally make empirical observations on responses over mineralization, rather than modelling the processes by which anomalous responses may form. Recent (Rich, 2016) and ongoing research at Highland Valley copper porphyry deposit, Central BC, (Chouinard et al., 2017), Lara VMS, Vancouver Island, BC (Bodnar et al., 2017) and the DO-18 Kimberlite in the Northwest Territories (Cayer et al., 2016) has indicated that many of the geochemical signals being observed at the surface may be the result of the incorporation of clastic materials from the deposit itself in the local till, rather than a vertical ion transfer process of metal from depth. There remains still an opportunity for detailed process-related research to model how anomalous responses form in till above concealed mineralization. This research needs to take into consideration depth, water table, surface geology, ion mobility and vegetation influences, amongst other factors. The necessity to understand the surface environment is paramount. Unravelling the pre-glacial, glacial and post-glacial development of the surface and sub-surface till environment is key to successful planning of geochemical surveys and interpretation of the geochemical results.

China

Geochemical exploration research through transported overburden continues to develop in China where a variety of covered terrains are tested in loess, arid sand dunes and valley and graben infill. Whilst Geogas was the focus of much of the early part of the 21st century (Wang et al., 2007), this has been superseded by the discovery of nanoparticles (Figure 4) in pressure-induced extraction of gas from soil horizons (Xiaojun et al., 2013; JianJin et al., 2009, 2010). This method uses a technique whereby nanoparticles of metals, metal oxides/sulphides/ silicates and alloys are collected onto metal grids for transmission electron microscopy (TEM) evaluation. As an exploration technique, the method directly dissolves the particles in acid during air extraction from the soil. The presence of these particles is perhaps not surprising given the reporting of nano-sized metal particles in nature and particularly the association with bacteria, which have been shown to produce nano-particulate metals as waste products from metabolic processes (Hough et al., 2008; 2011; Reith et al., 2010). However, potential mechanisms to transfer the particles from the ore to surface are uncertain. Transfer is currently postulated to be occurring by gaseous transportation or the “Geogas” of Wang et al. (2007); however, research needs to be placed in the context of surface development to understand if the particles are being locally generated or are the result of lateral transport. Ongoing research (Anand et al., 2017) has shown the association between nano-scale gold particles and organic material in pisoliths in the Yilgarn (Figure 5) indicating an integrated biological association.

Figure 4: Nano particles recovered from the Changkeng concealed gold deposit, Guangdong Province, South China. Modified after JianJin et al. (2009).
ANALYTICAL TOOLS IN UNDERCOVER EXPLORATION

Hydrocarbons

The application of hydrocarbons in non-petroleum mineral exploration remains contentious. Available commercial laboratories offering hydrocarbon analysis for mineral exploration have been reduced to two: Activation Laboratories (SGH); and Advanced Geochemical Imaging (AGI), with the closure of the Soil Desorption Pyrolysis group in Australia. The commercial OreHound© system (Luca, 2012), initially set up to collect hydrocarbons for subsequent analysis at Activation Laboratories, has subsequently been modified to remove the hydrocarbon collector (Townley, pers. comm., 2016). The two remaining methods differ widely in methodology and results. The AGI technique is a time integrated hydrophobic Gore-Tex© coated collector buried in the ground for ~30 days and subsequently analyzed by thermal decomposition GC-MS. Results are reported as individual organic compounds at ng/L concentration levels (Figure 6) (Noble et al., in press). Conversely the Actlabs methodology involves the solvent extraction, using hexane, of hydrocarbons directly from a soil sample with LC-MS. Classes of compounds rather than individual compounds are reported (Heberlein, 2010). Other adsorbent phases, including activated charcoal or kaolin have also been evaluated by various researchers, though none taken to successful commercial application. The former technique, dominantly used by the petroleum industry, has seen little application in non-petroleum mineral exploration outside of academic research (Rich, 2016; Noble et al., in press), however, it has shown promising results. Ongoing research has clearly shown the association of changing hydrocarbon signatures with low level changes in trace metal contents (Figure 7) (Cayer et al., 2016; Luca et al., 2008).

Genomics – Molecular Biology

It is estimated that within a gram of fertile soil there may be as many as 10 million living organisms (Blume et al., 2015) comprising 10s or even 100s of thousands of microbial species (Van Der Heijden et al., 2008) each sensing and interacting with the surrounding soil environment. Together, they are largely responsible for catalyzing biogeochemical cycling in soil, regulating the decomposition of minerals and organic waste materials, and the regeneration of soil nutrients and fertility.
Microorganisms are highly sensitive and responsive to chemical and physical changes in their environment. Subtle changes in metal bioavailability, for example, can have a dramatic impact on the composition and structure of microbial communities and their activity levels (Bier et al., 2015; Dell’Amico et al., 2008; Azarbad et al., 2015). In residual terrains, where chemical gradients related to mineral deposits are high, microbial community variability has been clearly linked to soil chemistry (Coker, 2010; Reith et al., 2015). Classical microbial fingerprinting techniques (PCR-DGGE, T-RFLP) (Wakelin et al., 2012) have demonstrated changes in bacterial communities in soils over a buried VMS deposit in the semi-arid desert of Australia. Likewise, soil microbial communities have shown responses in both taxonomic composition and metabolic potential (functional genes) to anthropogenic enrichments in elements such as Cu and As, specifically relevant to the exploration for Cu-Au porphyry deposits. High-throughput sequencing technologies, however, have transformed the analysis of soil microbial communities from such qualitative assessments of community membership and the relativity of abundance of individual genes to nearly quantitative mapping of entire microbial community genomes with capacity to assess community metabolic potential (Jansson, 2015). Application of modern sequencing technologies will allow the profiling of taxonomic diversity and metabolic potential of soil microbial communities across subtle and possible unsolvable geochemical gradients that have developed in soils in response to concealed mineralization. Given that each soil sample comprises thousands of microbial taxa, each of which contains hundreds to thousands of genes, the statistical power of this approach to identifying anomalies is unprecedented.

**DEPOSIT GEOCHEMICAL MODELS**

Deposit geochemical models continue to advance in the collection of multi-element geochemical datasets for numerous deposits, coupled with high quality geological mapping and alteration studies (Figure 8) (Halley et al., 2015). This information provides detailed input into the evaluation of multi-element geochemical datasets at both the lithogeochemical and surface sampling media levels.

![Figure 8: Multi-element geochemical model of trace element distribution in porphyry deposits (after Halley et al., 2015).](image)

On a broader scale, projects such as the CMIC Footprints Project (CMIC, 2017) are modelling the geochemistry of 3 mineral deposits (porphyry copper, unconformity uranium and Archean disseminated Au styles) in conjunction with the geology, geophysics, mineralogy and structure to develop integrated next generation exploration models.

**TECHNOLOGICAL ADVANCES**

**Fp-XRF and Other Portable Instruments**

Field Portable XRF has received large scale acceptance by the minerals exploration industry with numerous companies using the instruments routinely for the analysis of soils, stream sediments, rocks and drill core. In many instances the instruments are utilized as screening tools to differentiate between samples with elevated elements of interest contents versus samples with background contents for submission of the former for standard commercial aqua-regia or 4-acid digest coupled with ICP-OES and/or ICP-MS. Landmark publications (Hall et al., 2012; Hall et al., 2013) from the CAMIRO Project 10E01 and others (Fisher et al., 2014; Hall et al., 2014; Brand and Brand, 2014; Piercey and Devine, 2014; Ross et al., 2014) assessing the quality of fp-XRF results had an impact on both users and suppliers in identifying limitations of the instruments.
in routine exploration, in addition to guidelines on the use of the instruments. Since these reports, the instruments have effectively reached their zenith, with minor improvements in detection and data processing. Currently, fp-XRF has poor capabilities for the analysis of Au at the ppb levels typically encountered in exploration, although future improvements in field portable pre-concentration may result in an order of magnitude decrease in the detection of Au (low ppb; M. Lintern, pers. comm.). Novel work has been undertaken focusing on the use of pathfinders and lithogeochemistry from fp-XRF to assist with Au exploration (Arne et al., 2014; Benn et al., 2011). Despite the broad knowledge of fp-XRF detection, there is still a degree of misapplication with, for example, companies misleadingly reporting Au results which are little more than interference of Zn, As or W on Au.

Other field portable technologies are also becoming used in mineral exploration. Portable XRD (X-ray diffraction), LIBS (Laser-induced breakdown spectroscopy) and spectral SWIR (Short-wave infra-red) measurements are commonly used, although applications in mineral exploration are not widely published. The use of LIBS is particularly valuable as it has the ability to detect light elements that are not possible with fp-XRF. A recent global demand for Li has promoted that application of this method further, and it may become nearly as common as fp-XRF in the future.

Development of handheld FIR (far infra-red) spectral devices is just coming to market and these devices have significant benefit in the ability to analyze silicate phases that was not achievable with the shorter wavelength analyses. These field portable devices perhaps are the greatest change in geochemistry of the past 10 years; however, associated with this is the need to process the data rapidly and in conjunction with other results.

**Data Evaluation and Integration**

Scientific literature continues to extend the plethora of data evaluation techniques, many heavily dependent on advanced mathematics (e.g., Zou and Carranza, 2016, and articles therein), which whilst interesting case studies in their own right, using techniques such as fractal analysis, spatially weighted principal component analysis or bi-dimensional empirical mode decomposition analysis, generally fail to gain traction beyond the developers. This is in part a reflection of the intractable mathematics utilized in many of the techniques, but also the lack of access to the algorithms, hence reducing the potential for “real world” application and evaluation. In practice, considerable commercially generated data are still treated element by element focusing on the key commodity and extraction chemistry other than tweaks to current techniques or the broadening of existing methodologies across the complete range of commercial facilities. In practice the routine use of selective extractions and partial digestions is dominantly through junior companies, many of which lack specialist internal geochemical services.

With improvement in technology, additional applications of MLA (Mineral Liberation Analysis) have included the automated analysis of heavy mineral concentrates from till and other transported materials (Wilton et al., 2016). Perhaps one of the most advanced applications of MLA in industry applied to exploration is that utilized by Rio Tinto. It utilizes an MLA instrument connected to LA-ICP-MS to allow for identification of grains of interest using the MLA, with major element analysis, followed by LA-ICP-MS analyses using the major element analysis from the MLA to normalize the analytical data (Agnew, 2014).
stream sediments, along unconformities in transported sediments or from glacial till. In practice the work is an extension of the research undertaken from the late 1990s and early 2000s on kimberlite indicator minerals including morphology, survivability and chemistry.

Detailed trace element geochemistry of epidote and chlorite (Figure 9) has been demonstrated to have vectoring capability in the exploration for porphyry Cu-Mo-Au deposits (Cooke et al., 2014; Wilkinson et al., 2015). Similarly, a range of minerals, in particular apatite, (Bouzari et al., 2016; Mao, 2016) have shown value as indicators of differing styles of hydrothermal activity in porphyry systems and hence add value in detrital mineral studies.

![Figure 9: Plots of element concentration ratios in chlorite as a function of radial distance from the Batu Hijau centre. A, Ti/Sr ratio; C, Mg/Sr ratio (Wilkinson et al., 2015).](image)

**REGIONAL SCALE SURVEYS**

Regional scale geochemical data continue to become more readily, publically available and dominantly funded through pre-competitive government sources rather than by mineral exploration companies. These data are typically generated either with the purpose of promoting mineral exploration and have a relatively high density, or as environmental baseline datasets with relatively low sampling density. Recent examples include the low density geochemical survey of Europe (GEMAS project – Reimanns et al., 2014a, b) with sampling of agricultural soils at a density of 1 site/2500 km², the ongoing exploration geochemical scale survey (1 per 22 km²) of stream sediments in northern Chile (Sernageomin, 2015); the continental scale geochemical atlas of Australia (de Caritat and Cooper, 2016), and the ongoing regional scale geochemical mapping of China (Li et al., 2014). This latter project is undertaking sampling at a phenomenal density of 1 sample/km², increasing to 2 samples/km² in urban areas across the whole of China. Up to 376,679 samples had been collected and analyzed by late 2012 (Li et al., 2014). While the main aim of this project appears to be primarily directed at environmental studies (Zhang et al., 2015), the sample type, density of sampling and analytical methodologies will allow application of the sampling to mineral exploration. Many other countries, e.g., Colombia, continue to compile available government geochemical datasets with the intention of making the data publically available, in addition to producing geochemical atlases of the country (Figure 10).

**APPLIED GEOCHEMISTS**

Membership data from the Association of Applied Geochemists, (A. Arsenault, pers. comm., 2017) indicate that membership decreased by around 20% in 2013/2014. Of concern being the decrease in student numbers by 50% over the same period. Other associations have had similar number reductions following the global financial crisis and flow-on effects. This continues the trend previously reported (Cohen et al., 2007) of decreasing availability of students and future trained exploration geochemists, due to the lack of appropriate courses at university level. The initiation of new research groups, such as the Exploration Geochemistry Initiative at the University of British Columbia, whilst having a mission statement to generate the next generation of geochemists, is unlikely to exceed the number of geochemists being lost to industry, dominantly through retirement of an aging population.

**SUMMARY AND CONCLUSIONS**

Geochemistry remains at the forefront of mineral exploration as a primary tool along with geology and geophysics to identify potential mineral resources. Despite the limited financial resources for research and development as a function of repeated economic downturns over the past decade, there has been some developments, notably in the application of micro-analytical techniques and the application of mineral chemistry to mineral exploration, both in-situ minerals as well as detrital minerals. The development of potential biosensors and the reducing cost of microbial fingerprinting will enable much more research over the next decade of microbial geochemistry related to mineral exploration.

“The Big Data” concepts are only now starting to impact on mineral exploration; the availability of detailed photographic, hyperspectral, geophysical and geochemical data on drill core will require new tools to maximize and optimize the value of the data.

The development of potential biosensors and the reducing cost of microbial fingerprinting will enable much more research over the next decade of microbial geochemistry related to mineral exploration.

The supply of applied geochemists to industry appears to be on a continual downward trend. As the available consultants continue to retire, it will inevitably put pressure on available resources. Greater proactivity needs to be established by both industry and...
educational institutions to ensure that this deficiency does not eventually become a limiting factor in the minerals industry.

Figure 10: Regional scale geochemical map of Colombia compiled from multiple datasets by the Geological Survey of Colombia in collaboration with the MDRU, University of British Colombia, Canada (Perez et al., 2017).

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